CONFORMATIONAL EFFECTS ON THE CYCLOPOLYMERIZATION OF N-(p-BROMOPHENYL)DIMETHACRYLAMIDE

By

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To my parents
who through their love, encouragement, and sacrifices
gave their five children the opportunities
they never had

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The title compound, N-(p-bromophenyl)dimethacrylamide, was synthesized and then polymerized in the solid state by irradiation with cobalt-60 γ-rays. Spectral analysis of the resulting polymer indicated that the monomer cyclized completely in the polymerization and that a large percentage of both five- and six-membered rings was formed. The orientation of the double bonds in the crystal lattice was determined by single crystal X-ray diffraction analysis. In all cases the distances separating two potential intramolecular reactors were shorter than that separating the potential intermolecular reactors. It was concluded that the monomer crystallized in a conformation that would favor the cyclization reaction so long as the crystal lattice controlled the course of the polymerization. It was

also concluded that the percentages of five- and six-membered rings could not be predicted from the crystallographically-determined atomic positions. Electron spin resonance measurements on the irradiated sample indicated the radical centers generated by the irradiation were stable for more than 30 days. This persistence of the signal was probably an indication of the restricted mobility of these species in the crystal lattice.

When the radical-initiated solution polymerization of the monomer was performed at 50°C, a cyclopolymer containing predominantly the less stable ring size, the five-membered ring, was formed. Raising the reaction temperature to 114°C, however, increased the percentage of the thermodynamically-favored six-membered rings. Changes in the polarity of the solvent had little effect on the structure of the polymer. The appearance of a new imide stretching band in the infrared spectra of the monomer for the transition from solid to solution phase could be indicative of conformational changes upon dissolution.

An investigation into the relative stabilities of the various conformations available to the monomer was made using a Perturbative Configuration Interaction method with Localized Orbitals (PCILO). Conformers with a cis-trans and trans-trans orientation of the imide group were found that were fairly low in energy. Some energy lowering was observed for conformers in which the pi clouds of the monomer's two carbon-carbon double bonds could interact through space. One particularly low energy conformer was found by this investigation in which the two β-carbons of the double bonds were fairly close in space. If the monomer existed predominantly in this conformation in solution or had easy access to it by a rotation around a single bond, radical initiation of that conformer and a subsequent fast cyclization would result in the formation of five-membered rings in the backbone of the polymer.

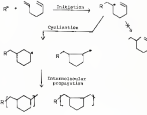
CHAPTER I
INTRODUCTION

Cyclopolymerization - General Concepts

The polymerization of monomers containing more than one carbon-carbon double bond per molecule is known to result generally in the formation of either a linear polymer containing unreacted double bonds or a crosslinked, three-dimensional polymer network. However, it has been observed that certain nonconjugated dienes do not react in either of these two ways. In 1951, Butler and Ingle[1] reported that the polymerization of diallyl quarternary ammonium salts resulted in the formation of linear soluble polymers containing little or no residual unsaturation. The mechanistic explanation offered by Butler[2] and Butler and Angelo[3] proposed an alternating intramolecular-intermolecular chain propagation reaction or, as it is now more familiarly known, cyclopolymerization. These addition reactions were characterized by the formation of cyclic units along the backbone of the polymer chain.

With the work of Butler and co-workers providing the impetus a considerable investigative effort has since been expended in this field. Marvel and Vest[4, 5] very quickly extended Butler's discovery to the polymerization of 1,6-heptadiene-2,6-dicarboxylic acid, its methyl and ethyl esters and its nitrile, all of which yielded linear, soluble polymers that were essentially free of unsaturation. Field[6] was able to demonstrate in his study of the polymerization of 2,6-diphenyl-1,6-heptadiene that thermal, free radical, cationic, anionic, and Zeigler initiation could all result in the production of polymers that are completely cyclized. Polymers containing heterocyclic rings along the backbone have been formed from monomers containing nitrogen (e.g. N-substituted diallylamines[7, 8] and N-substituted dimethacrylamides[9]), oxygen (e.g. methacrylic anhydride[10] and divinyl acetals[11]), sulfur (e.g. S,S'-divinylmercaptals,[12, 13] di-2-chloroallyl sulfide,[14] and di-2-chloroallyl sulfone[14]), silicone (e.g. substituted diallyl silanes[15-20]), phosphorus (e.g. diallylphosphine oxides[21, 22]), and germanium (e.g. diallyl germanium derivatives[16]). Other bifunctional molecules such as acetylenes, aldehydes, isocyanates, epoxides, and nitriles have led to the formation of cyclopolymers upon proper initiation of polymerization. Isolation of products from the polymerization of nonconjugated dienes has produced evidence of the existence of cyclopolymers containing five-membered rings, six-membered rings, even larger ring sizes, and, in some cases, bicyclic structures. Reviews of cyclopolymerization processes were published early by Butler[23] and Marvel[24] and then later by Butler,[25] Gibbs and Barton,[26] Matsoyan,[27] Corfield, Aso, and Butler,[28] and Butler.[29]

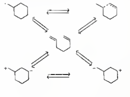
As a result of these fairly intensive investigations the general course for the cyclopolymerization of nonconjugated 1,6-dienes is now widely accepted as that shown below:



* = cation, anion, or free radical

However, no one totally satisfactory mechanism exists at present that can adequately account for all the experimental observations. It is unlikely that the large number of molecules that will cyclize completely upon initiation of polymerization do so as a result of simple statistical probability alone.

In an attempt to explain the sometimes contradictory experimental observations, two somewhat different mechanistic explanations have been proposed. In 1960, Butler[30] first postulated that there could exist a through-space nonconjugated electronic interaction between the double bonds of the 1,6-dienes as demonstrated below.



Such an interaction, should it exist in either the ground state or the excited state, would be expected to provide a more energetically favored pathway in the form of reaction by cyclopolymerization rather than by linear propagation involving only one of the double bonds per molecule. The facile cyclization reaction thus expected would be consistent with a concerted process. If this nonconjugated interaction did exist it might also be possible to observe bathochromic shifts in the ultraviolet spectra of these monomers and a corresponding lowering of the energy of activation for the cyclization step.

The second mechanistic proposal, that of a steric interaction, was first formulated by Gibbs and Barton[26] in 1967, although the importance of steric factors had been noted previously by other investigators. This steric interaction theory hinges on the proposal that steric factors alone control the course of the reaction. After initiation of the first double bond, the second double bond should be frequently presented to the reactive site in a conformation favorable for reaction. In addition, the second carbon-carbon double bond would serve to sterically shield the reaction site from the incoming monomer, thereby decreasing the probability for linear propagation. Once formed, the cyclized radical would be much less sterically hindered and could participate in an intermolecular propagation reaction. As was pointed out by the authors[26] this theory would predict no difference in the activation energies for the two steps.

The experimental observations to date do not consistently support either of the two mechanisms. Until recently there was little experimental evidence for ground state interactions between the two double bonds in the nonconjugated dienes. However, a photoelectron spectroscopic study,[31] in 1976, reported that a conformation of 1,5-hexadiene in which the two double bonds are crossed (I) is more stable by 2.3 kcal/mole than the open chain conformation (II). Bathochromic shifts have been reported in the ultraviolet spectra of methacrylic anhydride,[32] a series of allyl silanes,[33]

I

II

and certain tetraenes.[34] However, a series of alkylcycloalkenes[35] and unsymmetrical heptadienes[36] failed to show such shifts. The shifts exhibited by methacrylic anhydride have been alternatively explained[37] by an electronic stabilization through resonance of the non-bonded electrons on the anhydride oxygen with the carbonyl group. When an open-chain system does demonstrate bathochromic shifts, it should be assumed, in accordance with the Franck-Condon principle,[38] that the molecule is preoriented in a conformation that would favor the occurrence of that electronic transition. There are, however, many monomers that cyclopolymerize for which there is presently no evidence for such an excited state interaction. In most cases for which data are available the energy of activation is usually higher than that for intermolecular propagation. Yet k_c/k_i, the ratio of the rate constant for cyclization to the rate constant of initiation, is usually greater than one.

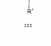
The case for the steric interaction theory is equally uncertain. A pendant group on the β-carbon of monovinyl monomers reportedly has an effect on the propagation and termination rate constants. One would expect, therefore, that the rate of intermolecular reaction for a 1,6-diene would be lower than that of a similar monomer that has less than five atoms in the pendant group. A large degree of cyclization might be expected, though, if the pendant group shielded the propagating radical from the approach of a second monomer molecule. A comparison of the rate constants of polymerization of methyl methacrylate and n-butyl methacrylate[39] indicates little effect of the length of these pendant groups on the β-carbons on propagation and termination. Nevertheless, while N-methyldimethacrylamide readily undergoes radical initiated cyclopolymerization, its monovinyl counterpart, N-methyl-N-isobutyrylmethacrylamide, does not polymerize under identical conditions.[40] It has also been reported[41] that 2,6-dicyano-1,6-heptadiene polymerizes nearly 590 times faster than the analogous mono-ene, 2-cyano-1-heptene.

Yet another weakness of the steric control theory is that a very rapid rotation of the pendant group would be necessary to exclude all intermolecular propagation. Cyclopolymerization is still observed at low temperatures and high monomer concentrations.

Background of this Study

In 1971, Butler and Myers[40, 42] reported an investigation into the spectroscopic and polymerization characteristics of a series of N-substituted dimethacrylamides. They were attempting to find some experimental basis for the proposed "electronic interaction" theory by comparing the ultraviolet and nuclear magnetic resonance spectra of the dimethacrylamides with those of their mono-ene counterparts, the N-isobutyrylmethacrylamides. If there were such an interaction, its importance in governing the course of the polymerization reaction should certainly hinge on the conformation of the molecule. They predicted that there should exist two primary factors determining the orientation of the two carbon-carbon double bonds with respect to each other: the conformation of the imide group and that of the methacryl group.

In order to allow maximum delocalization of the pi cloud the imide group might be expected to orient in at least one of three possible coplanar arrangements: cis-cis (III), cis-trans (IV), or trans-trans (V). Of these three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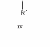
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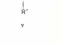
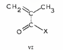
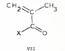

V

conformers one would predict that the trans-trans orientation would be the least likely since the carbonyl groups are parallel to each other and the electrostatic repulsions between them should raise the energy of that conformation. Dipole measurements on diacetamide ($R = CH_3$, $R' = H$) and N-methyldiacetamide ($R = R' = CH_3$) indicate that these simple imides exist in the cis-trans orientation.[43] As one increases the steric requirements of R from $-CH_3$ in diacetamide to that of the even bulkier methacryl groups, there should be an even stronger preference by the dimethacrylamides for the cis-trans orientation.

The second consideration is that of the conformation of the methacryl groups. Maximum delocalization of the pi cloud should once more favor a coplanar arrangement of the unsaturated groups. There are two such arrangements possible for the carbon-carbon double bond and the carbonyl group, the s-cis (VI), and the s-trans (VII). According



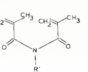
VI



VII

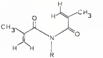
to Butler and Myers[42] the s-trans orientation should be of lower energy. If, however, the carbonyl substituent, X, is large and steric repulsions prevent coplanarity of the carbon-carbon double bond and the carbonyl group, the s-cis conformation would be favored.

From basic electronic considerations the dimethacrylamides would, therefore, be expected to exist predominantly with a cis-trans orientation around the imide group and the methacryl group in an s-cis or s-trans orientation. However, conformations such as (VIII) below, which would favor nonconjugated interactions, can be achieved only by twisting the methacryl group out of a coplanar arrangement.



VIII

Examination of the ultraviolet spectra of the monomers as a probe into their conformation[42] resulted in much more complicated spectra than expected. The interaction of the carbonyls through the nitrogen was the major factor affecting the observed transitions. The variations in chemical shift with solvent in the nuclear magnetic resonance spectra of the compounds were also used to investigate the conformations of the molecules. The primary effect that was observed was correlated to changing the nitrogen substituent, an alteration that almost certainly triggered conformational changes of the imide group. It was proposed that these observed shifts would be consistent with a cis-trans orientation around the imide and s-trans orientation for the methacryl group as shown by (IX). The vinyl proton would then be located in a region where it would be shielded by the carbonyl of the second methacryl group. Any changes in the conformation of the imide group

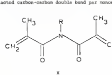


IX

would alter the shielding of the vinyl protons and lead to subsequent chemical shifts in the pmr spectra similar to those observed. It was therefore concluded that this cis-trans isomer could be a major contributing conformer for the dimethacrylamides they studied.

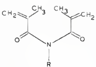
As an additional probe into the conformation of the amides Butler and Myers[40] further postulated that if a 1,6-interaction did exist in these dienes then it might persist in the solid state when the monomer crystallized out. Therefore a solid state polymerization of these monomers would lead to cyclopolymer only if the double bonds were preoriented in a conformation favorable for cyclization.

Calculations performed by Treloar[44] indicate that the most probable distance for a one-dimensional five-carbon link similar to that shown in conformer (X) is 4.95 Å. Such a large distance in the crystal lattice would likely inhibit the cyclization reaction. Bond formation would necessarily involve a considerable migration of the second double bond to the reactive site, a degree of freedom that does not exist to a large extent in the solid state. Therefore, if the monomer crystallized out predominantly in a conformer such as (X) the solid state polymerization should only lead to crosslinked polymer or to a linear polymer with one unreacted carbon-carbon double bond per monomer unit.



X

On the other hand, Butler and Myers made the assumption that if cyclization were the predominant mode of propagation in the solid state, the intramolecular double bonds should be preoriented in the crystal lattice either as shown in (VIII) or (XI) or in some conformation approximating one or both of these. The existence of that conformation in the solid state, while apparently improbable



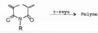
XI

elsewhere, could possibly be accounted for on the basis of a homoconjugative, through-space interaction of the double bond.

A summary of the results they obtained upon irradiation of the monomers with γ-rays from a cobalt-60 source is given in Table 1. Since the structures of the polymers obtained were similar to those obtained by solution polymerization they concluded that the radiation-induced polymerization probably propagated by a radical mechanism. It

Table 1

Radiation- Induced Polymerization of N-Substituted Dimethacrylamides



R	Conversion[a] %	[η]	5-Membered %	6-Membered %	Uncyclized %
-H	4.0[b]	Insol			
	Insol[c]				
$-CH_3$	4.3[b]	0.062	70	30	—
	100[c]	0.07			
$-C_6H_5$	0.5[b]	--	100		
	22[c]	0.06			

[a] G.B. Butler and G.R. Myers, J. Macromol. Sci.-Chem., A5(1), 135 (1971).

[b] Irradiated for 26.5 hours at a dose rate of 0.5 Mrad/hr; total dose = 13 Mrad.

[c] Irradiated for 65.3 hours at a dose rate of 1.4 Mrad/hr; total dose = 91 Mrad.

had been assumed that if the crystal structure were a major factor in the cyclization step then the polymer obtained would have a simple structure. Contrary to free-radical initiation which produced polymers consisting nearly exclusively of five-membered rings, the solid state polymers had a more random distribution of rings—there was a detectable proportion of five- and six-membered rings. Therefore, even though the monomer appeared to be preoriented in a manner that highly favored the cyclization step, it was concluded that the crystal lattice must not control the direction of the cyclization step.

Statement of the Problem

The work reported by Butler and Myers[40, 42] served to pose yet another question—that concerning the actual processes occurring in the solid state polymerization of the dimethacrylamides. Does the crystal actually control the course of the reaction and is the monomer actually preoriented in a conformation favoring cyclization? Is the presence of both five- and six-membered rings indicative of random processes occurring in the crystal or would they be expected if a greater knowledge of the monomer conformation were available? Exactly how much can these solid state processes be extrapolated to the solution processes?

In an attempt to answer these questions an X-ray diffraction study was undertaken as a probe into the crystal structure and the resulting solid state processes. The monomer, N-(p-bromophenyl)dimethacrylamide, was chosen as the model compound for the study. It was postulated that since the only change in structure from that of N-phenyldimethacrylamide was the substitution of a bromine atom para to the nitrogen, the monomer might also form cyclopolymer to a high degree with initiation by free radicals and with γ-rays from a cobalt-60 source. The purpose of the bromine substitution was to provide a somewhat easier solution of the structure using X-ray heavy atom techniques.

After synthesis of the monomer and polymerization by γ-irradiation the structure of the polymer was investigated. The structure of the crystalline monomer was determined by an X-ray diffraction study and correlations to the polymerization behavior made. The polymerization processes were further investigated using electron spin resonance techniques.

The solution behavior of the monomer was also investigated. Infrared spectroscopy was used to probe monomer conformational behavior in solution. Polymerization of the monomer was initiated using free radical and anionic catalysts and structures of the resulting polymer were studied.

If the monomer did have many conformations available to it, the relative importance of these conformations would be useful in predicting its most probable orientation(s).

Therefore an investigation into the relative energies of prominent conformations available to N-(p-bromophenyl)-dimethacrylamide was also undertaken using a quantum mechanical Perturbative Configuration Interaction with Localized Orbitals (PCILO) method.

CHAPTER II
EXPERIMENTAL

Equipment and Data

All temperatures are reported uncorrected in degrees Celsius. All pressures are reported in millimeters of mercury. Melting points were determined in capillary tubes with a Thomas-Hoover capillary melting point apparatus. The elemental analysis was performed by Galbraith Laboratories, Inc. in Knoxville, Tennessee.

Infrared spectra were recorded on either a Beckman IR-10 or a Beckman IR-8 Spectrophotometer. Solution infrared spectra were recorded on a Beckman IR-10 using matched 0.1 mm potassium chloride cells. The absorption band positions reported are given in wavenumbers (cm^{-1}).

Proton magnetic resonance (pmr) spectra were recorded on either a Varian Associates Model A-60, 60 MHz spectrophotometer, or a Varian Model XL-100, 100 MHz instrument. Chemical shift values for ^{1}H resonances are reported in δ units relative to tetramethylsilane (TMS) at δ 0.00.

Gel permeation chromatography (gpc) was performed on a Waters Associate Model 6000A liquid chromatograph with a Model 440 absorbance detector. For the polymer samples studied μ-styragel columns having pore sizes 10^3 Å and 10^2 Å were used in series. The eluting solvent was Mallinckrodt SpectrAR grade chloroform.

Electron spin resonance (esr) spectra were recorded on a Varian E-3 EPR recording spectrometer with a field modulation of 100 Kcycles/sec. The power level of the spectrometer was 3.20 mw and the crystal current was 300 ma.

Monochromatic ultraviolet light irradiation was obtained from a 2500 w Mercury Xenon lamp which was contained in a Schoeffel LN 152N/2 lamp housing. The output beam was deflected through a Schoeffel LHA 165/2 prism into a Schoeffel GM 250 high intensity monochromator.

All solvents were commercial reagent grade and were used as received unless otherwise noted. Polymer nonsolvents were technical grade and were filtered before use.

Monomer Synthesis

N-(p-Bromophenyl)methacrylamide

This compound was prepared by the method reported by Butler and Myers[42] for the synthesis of N-phenylmethacrylamide. In a typical run, a solution of 84.0 g (0.488 mole) of p-bromoaniline [Eastman Organic Chemicals], 400 ml absolute diethyl ether (which had been dried by distilling from lithium aluminum hydride), and 49.4 g (0.488 mole) of redistilled triethyl amine [Matheson, Coleman, and Bell] were placed in a 1-liter, three-necked flask fitted with a mechanical stirrer, constant-pressure addition funnel, reflux condenser and drying tube. While the solution was being stirred at 0-5° a solution of 51.0 g (0.488 mole) redistilled methacryloyl chloride [Aldrich] and 50 ml absolute diethyl ether was added dropwise through the addition funnel over a three-hour period. A thick white solid precipitated during the addition and stirring was continued overnight. Upon the addition of 500 ml water to the mixture the white solid dissolved and two distinct layers were formed. After separation of the two layers, the non-aqueous layer was washed first with two 100 ml portions of 1N hydrochloric acid and then with two 100 ml portions of 10% aqueous sodium carbonate. The solution was then dried overnight with anhydrous magnesium sulfate. After filtering off the drying agent, diethyl ether was removed by a rotary evaporator. Recrystallization of the thick white precipitate twice from acetone-hexane cosolvents yielded 72.2 g (62%) of white, fiber-like crystals, m.p. 117-118°. The ^1H nmr spectrum ($CDCl_3$) exhibited resonances at δ: 2.10 (s, broadened, 3), 5.45 (s, broadened, 1), 5.80 (s, broadened, 1) and 7.45 (m, broadened, 5). The infrared spectrum (Nujol) showed absorbances at: 3315 (m), 1670 (m), 1615 (ms), 1590 (m), 1500 (s), 930 (s), and 820 (s).

N-(p-Bromophenyl)dimethacrylamide

The monomer was synthesized according to the method reported by Butler and Myers[42] for N-phenyldimethacrylamide. Before assembling, all glassware was washed and baked overnight in an oven at 110°. After assembling, the set-up was flamed out under a steady stream of nitrogen which was dried by bubbling through sulfuric acid and then passing through a drying pistol filled with potassium hydroxide and calcium sulfate. The solvent, tetrahydrofuran, was distilled from lithium aluminum hydride immediately prior to use. Sodium hydride was washed very quickly with hexane to remove the mineral oil in which it was dispersed.

Into a 250 ml three-necked round-bottomed flask equipped with a nitrogen-inlet, pressure-equalizing addition funnel, mechanical stirrer, reflux condenser, and drying tube was placed the solid sodium hydride remaining after washing with hexane 5.0 g of a 50% mineral oil dispersion [PCR, Inc.] and 35 ml of tetrahydrofuran. While the mixture was stirred under a steady stream of nitrogen, a solution of 23.85 g (0.100 mole) of N-(p-bromophenyl)methacrylamide (as prepared above) and 40 ml tetrahydrofuran was added dropwise through the addition funnel over a three hour period. This reaction resulted in the formation of a grayish-green slurry which was allowed to stir at room temperature for an additional half-hour.

Into a 300 ml three-necked round-bottomed flask assembled and equipped as above was placed 11.5 g (0.110 mole) freshly distilled methacryloyl chloride and 500 ml tetrahydrofuran. The sodium salt of N-(p-bromophenyl)methacrylamide prepared above was transferred to the addition funnel and added dropwise with stirring and under a steady stream of nitrogen over a four hour period. The round-bottomed flask was cooled to 0-5° during the addition.

After an additional hour of stirring a grayish solution with a white precipitate remained. To this mixture 10 ml methanol was slowly added until gas evolution ceased. The mixture was poured into 300 ml rapidly stirring hexane and the white precipitate was suction filtered. After removing the solvent with a rotary evaporator the remaining thick white precipitate was recrystallized twice from 95% ethanol to yield 11.53 g (37.6%) of white needle-like crystals, m.p. 105-106.5°.

The ^1H nmr spectrum ($CDCl_3$) exhibited resonances at δ: 1.95 (s, split, 6), 5.55 (m, broadened, 4), and 7.25 (m, sharp, 4). The infrared spectrum (KBr) showed absorbances at: 3000 (w), 1705 (s), 1690 (s), 1620 (m), 1490 (m), 1450 (m), 1315 (s), 1165 (s), 820 (s), and 500 (s).

Anal. Calcd. for $C_{14}H_{14}BrNO_2$: C, 54.56; N, 4.54; H, 4.57; Br, 25.92; O, 10.41. Found: C, 54.70; N, 4.49; H, 4.50; Br, 26.08.

Solid State Polymerization

Initiation by Gamma Rays

Calibration of the cobalt-60 source was accomplished by the use of Fricke dosimetry[45] which measures optically the conversion of $Fe^{+2} \rightarrow Fe^{+3}$ after periods of γ-irradiation. By measuring the absorbance of the Fricke solution at 304 nm (λ_{max} for Fe^{+3}) and using the data obtained in solving the two equations below the dose at that position could be determined. The dosimetry and subsequent monomer irradiations were performed in 10 mm Pyrex tubes. The design and construction of the irradiator have been previously described in the literature.[46]

$$[\mathrm{Fe}^{+3}] = \frac{\mathrm{O.D.}}{\varepsilon \times l} = \frac{\mathrm{O.D.}}{\varepsilon_1 [1 + 0.007\ (t_2 - t_1)]}$$

$$\mathrm{Dose} = \frac{1000\ \frac{\mathrm{Krad}}{\mathrm{Mrad}}\ [\mathrm{Fe}^{+3}]}{15.5 \times 1.036 \times 1.024 \times 10^{-3}\ \mathrm{mol/dm^3\ Mrad}}$$

where O.D. = optical density at 304 nm

$\varepsilon_1 = 2193 \pm 6\ \mathrm{dm^3/mol\ cm}$ at 25°

The irradiations were first performed as described by Butler and Myers.[40] The crystalline monomer, N-(p-bromophenyl)dimethacrylamide, was placed in a 10 mm Pyrex tube, evacuated to 10^{-5} mm and sealed. The tube containing the monomer was then placed in a sample holder adjacent to the source and irradiated for 60 hours (dose of 76.2 Mrad). At the end of that period changes in the crystals were not usually discernable. After continuing the irradiation time to 116 hours (total dose of 129.9 Mrad) the tube was left in the dark for six days to allow time for polymerization to occur. At the end of that period the tan crystals dissolved easily in acetone and the resulting solution was slowly dripped into 400 ml rapidly stirring hexane. The fine white solid that precipitated was collected by suction filtration through a sintered glass funnel. The precipitation process was repeated once more and drying 24 hours in vacuo yielded 0.161 g (16.1% conversion) of a fine white static powder, softening point, 185-193°.

The polymerization was repeated except that the monomer was exposed to ~2 Mrad of γ-irradiation at liquid nitrogen temperature (-196°). After allowing the reaction to proceed for 30 days, the evacuated tube was opened and the solid was treated as above. Dripping the acetone solution into hexane, however, yielded no isolable precipitate. The pmr of the white powder remaining after evaporation of the solvent was consistent with that of the monomer except for a few small peaks in the upfield region that would be consistent with less than 2% polymer.

Initiation by Ultraviolet Irradiation

The wavelength of maximum absorption of a 5×10^{-4} M solution of N-(p-bromophenyl)dimethacrylamide in diethyl ether was determined with the aid of an ultraviolet spectrophotometer to be ~220 nm. This, then, was chosen to be the wavelength of irradiation.

The crystalline monomer was then placed in a 21 mm o.d. quartz tube which was joined to a Pyrex section by means of a graded seal. After connecting to a high vacuum line the tube was evacuated to 10^{-5} mm and sealed.

The tube was then centered in the ultraviolet beam and rotated about its axis during 40 hours of irradiation. There was no visible change in the appearance of the solid at the end of the irradiation. After allowing several days for post-polymerization the tube was opened and the white solid was dissolved in acetone. Dripping the solution into rapidly-stirred hexane did not result in the formation of a precipitate. Evaporation of the solvent resulted in a nearly complete ($\sim$99%) recovery of monomer. The pmr showed no evidence of polymerization in the isolated solid.

X-Ray Diffraction Study

Single crystals of the monomer were grown by dissolution in absolute diethyl ether. The solution was then placed in a 20 ml beaker which was covered tightly with aluminum foil. One small hole in the foil allowed relatively slow evaporation of the monomer and formation of colorless rectangular single crystals.

Geometric data collection was performed using first Weissenberg and then precession X-ray photographic techniques.[47-49] A crystal was selected and mounted with paraffin wax on a glass fiber which was then fastened in a goniometer head. After aligning the crystal in the X-ray beam of a Weissenberg camera rotation photographs were made and the crystal symmetry was determined to be orthorhombic mmm. Indexing of the reflections, accomplished through the use of a Weissenberg festoon template, eliminated all space groups but Pbca and Pcca. Choice between these two groups was impossible with the Weissenberg data because the limiting conditions for reflections that would distinguish between the two was based on the axis (okl) about which the crystal was rotated. Since the only way data could be obtained for this axis on a Weissenberg camera would involve remounting the crystal on the glass fiber in a different orientation and perform all the centering and indexing once more, it was decided that the space group could be determined more easily through the use of the precession camera which allows one to map out the reciprocal lattice directly on film.

The crystal was re-centered in the X-ray beam of a precession camera and zero, first, and second level photographs were made for two orientations of the crystal. Comparison of the level shots and observation of the systematic absences yielded evidence for three perpendicular glide planes. Changing of the arbitrary axes names to one consistent with standard crystallographic notation resulted in the determination of the space group to be Pbca. Preliminary cell constants were determined from the axial repeat distances.

Each photograph was examined for possible evidence of polymerization occurring under the influence of the X-ray irradiation during geometric data collection. The diffuse rings expected if polymer had been forming did not appear.

The density of the crystals was measured by the flotation technique[50] and was in good agreement with that calculated for 8 molecules/unit cell. The specific gravity of the flotation liquid was measured to ± 0.01 with a precision hydrometer.

A suitable crystal was then mounted on the end of a glass fiber and centered on a Syntex $P\bar{1}$ diffractometer. After centering fifteen intense reflections and selecting an indexing consistent with the preliminary photographs, accurate cell constants were obtained from a least-squares fitting of 2θ, Ω, χ, and Φ (the four angles of a four-circle diffractometer) for these reflections. Pertinent crystal data are summarized in Table 2.

The intensity data were collected at ambient temperature using copper $K\alpha$ radiation ($\lambda = 1.5418$ Å). All unique reflections up to a limiting 2θ value were measured using a variable speed $\theta - 2\theta$ scan technique. The scan rate was determined from a fast three-second counting scan of the reflection peak. The rate varied linearly from 1°/minute for a counting rate of 150.0 c/sec or less up to 24°/minute for counting rates of 1500.0 c/sec or more. The intensity, I, is defined by the following equation:

$$I = (\text{scan rate})\left[\text{total scan counts} - \frac{\text{background counts}}{\text{background to scan ratio}}\right]$$

Intensity peaks were scanned from 1° below $K\alpha_1$ to 1° above $K\alpha_2$. Background count measurements were made at the limits of each scan. For each reflection the estimated standard

Table 2

Crystal Data for N-(p-Bromophenyl)dimethacrylamide

Parameter	Data
Symmetry	Orthorhombic
Space Group	Pbca
Color	Colorless
Crystal dimensions, mm	0.028 x 0.134 x 0.103
Measured density, g/cm^3	1.492
Calculated density, g/cm^3	1.489
Z(no. molecules/unit cell)	8
Conditions limiting possible reflections	hkl (No conditions)
	0kl k=2n h00 (h=2n)
	h0l l=2n 0k0 (k=2n)
	hk0 h=2n 00l (l=2n)
Molecular weight, g/mole $C_{14}H_{14}BrNO_2$	308.20
2θ(max), degrees	115.0
Number of observed reflections	1162
Number of unobserved reflections	707
Cell Dimensions	
α = β = γ, degrees	90.0
a, Å	29.727
b, Å	8.561
c, Å	10.792
Volume, Å^3	2746.49

deviation, σ(I), was calculated as follows:

$$\sigma(I) = [\text{total scan counts} + \frac{\text{background counts}}{(\text{background to scan ratio})^2}]^{1/2}$$

Changes in the system were monitored by measuring four standard reflections after each 96 intensity measurements. Reflections with an intensity greater than 2σ(I) were considered "observed" and were used in subsequent calculations. The reflections where $I < 2\sigma(I)$ were marked by a minus sign and were not used further in the calculations. Corrections for Lorentz-polarization were made by the following calculation. To obtain a set of observed

$$\frac{1}{LP} = \frac{\sin 2\theta}{(1 + \cos^2 2\theta)}$$

structure factors (F_{obs}'s) the monochromator was assumed to be 50% perfect crystal and 50% mosaic crystal.

Scattering factors for the atoms in the monomer were obtained from the following sources: bromine, oxygen, nitrogen, and carbon from International Tables[51] and those for hydrogen provided by Stewart, Davidson, and Simpson.[52] The values for bromine were corrected for anomalous dispersion of the copper Kα irradiation. The overall temperature factor and the natural log of the scale factor were estimated from a Wilson plot.[53] The initial choice of a centric or acentric space group was based on calculated intensity statistics.[54]

Since the monomer contained a heavy atom (bromine) the approximate positional coordinates were determined using a Patterson function[55] of the following form.

$$P(UVW) = \frac{2}{V} \sum_{h=0}^{\infty} \sum_{k=-\infty}^{\infty} \sum_{l=-\infty}^{\infty} |F(hkl)|^2 \cos 2\pi\ (hU + kV + lW)$$

The phase of each reflection, α (hkl), was then determined from the heavy atom approximation. The positions of the other atoms were then sought by the use of Fourier syntheses[55] of the form

$$\rho(XYZ) = \frac{2}{V} \sum_{h=0}^{\infty} \sum_{k=-\infty}^{\infty} \sum_{l=-\infty}^{\infty} |F(hkl)| \cos 2\pi\ [(hX + kY + lZ) - \alpha(hkl)]$$

The positions of all the non-hydrogen atoms were located using Fourier syntheses in an iterative fashion with the positions of the previously located atoms being used as a starting set for the next phase determination and Fourier synthesis.

An overall scale factor was calculated so that the sum of F_{obs} equaled the sum of F_{calc}. The model structure was then refined by a least-square minimization[55] of the function

$$\text{Residual} = \Sigma w(||F_{obs}| - |F_{calc}||)^2$$

where

$$w^{1/2} = F_{obs}/F_{low} \quad \text{if } F_{obs} < F_{low}$$

$$w^{1/2} = 1 \quad \text{if } F_{low} \leq F_{obs} \leq F_{high}$$

$$w^{1/2} = F_{high}/F_{obs} \quad \text{if } F_{high} < F_{obs}$$

The refinement initially used isotropic and then used anisotropic thermal parameters of the form

$$\exp\ [-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)]$$

After six cycles of anisotropic least-square refinement a difference Fourier synthesis was calculated to locate the positions of the hydrogen atoms. These positions were included in the subsequent least-squares calculations. The reliability index, R, was calculated by the following:

$$R = \frac{\Sigma||F_{obs}| - |F_{calc}||}{\Sigma|F_{obs}|}$$

An outline of the scheme of structure refinement is given in Table 3.

The calculations were performed on an Amdahl 470 V6 computer using programs written or modified by Dr. G.J. Palenik of the University of Florida, Center for Molecular Structure.

Table 3

Structure Refinement of N-(p-Bromophenyl)dimethacrylamide

Parameter	Data
Initial R	0.26
No. cycles FMLSQ isotropic thermal parameters H's not included	3
R after FMLSQ	0.17
No. cycles BDLSQ anisotropic thermal parameters H's not included	6
R after BDLSQ	0.077
No. cycles BDLSQ anisotropic thermal parameters H's included but not refined	3
R after BDLSQ	0.068
No. cycles BDLSQ anisotropic thermal parameters H's included and refined	9
Final R	0.058

Electron Spin Resonance

Polycrystalline Samples

Sample cells similar to those described by Adler, Ballantine and Baysal[56] were used for the irradiation of the monomer. The narrow portion of the cell was made of Amersil quartz, however, and was joined to the Pyrex portion by a graded seal. The crystalline monomer was placed in the wide end of the tube which was then evacuated to 10^{-5} mm and sealed. After irradiation with 2 Mrad of γ-rays at -196° the narrow end of the tube was annealed with a blow torch to remove the color centers in the tube. At the same time the sample was being kept cold by immersion of the wide end in liquid nitrogen. The sample was then shaken into the annealed portion of the tube and the ESR spectra were recorded at room temperature over a time span of one month. The tube was then opened to the atmosphere and the spectra recorded over a period of several days to measure the effect of oxygen on the spectra.

Solution Polymerizations

Free Radical Initiations

Before use all glassware was cleaned, rinsed with acetone, and dried in a 100° oven overnight. Benzene was reagent grade and was purified by shaking with sulfuric acid and distillation immediately prior to use. Dimethylformamide was also reagent grade and was purified by shaking with potassium hydroxide and distillation from calcium oxide immediately prior to use.

In a typical experiment, 15 ml of a 0.5 M solution of N-(p-bromophenyl)dimethacrylamide containing 1% recrystallized azobisisobutyronitrile (AIBN) was placed in a heavy walled Pyrex polymerization tube. The tube was then connected to a high vacuum line and, through a series of freeze-thaw cycles, was evacuated to 10^{-5} mm and sealed. The tube was then placed in an oil bath which was maintained at a constant temperature for the specified time. The polymer was precipitated by dripping slowly into a rapidly-stirred nonsolvent. The polymer was collected by suction filtration through a sintered glass funnel and dried to a constant weight in a 60° oven. To obtain samples for spectral studies, the polymer was dissolved and reprecipitated and dried to a constant weight. Some characteristics of the individual polymerizations are discussed below.

Polymerization in dimethylformamide. The polymerization was effected by heating in an oil bath which was maintained at 56° for 22 hours. A static white powder (0.274 g) was obtained after precipitating in a 1:1 mixture of hexane and diethyl ether. The polymer obtained was soluble in most common organic solvents at room temperature.

Polymerizations in benzene. The polymerizations were carried out by heating two identically filled sealed polymer tubes in oil baths which were maintained at 58° and 114° for 24 hours. After precipitating into a 1:1 mixture of hexane and diethyl ether and drying to a constant weight 0.340 g of polymer was collected from the former and 0.276 g from the latter polymerization. Both polymers were atatic white powders and were soluble in most common organic solvents.

Anionic Initiation

Before assembly all glassware was cleaned, rinsed with acetone, and dried in a 110° oven overnight. After cooling the glassware was assembled and flamed out under a steady stream of dry argon. Tetrahydrofuran used was reagent grade and before use was purified by shaking with potassium hydroxide and distilled from lithium aluminum hydride.

Into a 50 ml round-bottomed three-necked flask equipped with an argon inlet, drying tube, and magnetic stirrer was distilled directly 25 ml dry tetrahydrofuran. After disconnecting the distillation apparatus 1.2 g (0.0037 mole) N-(p-bromophenyl)dimethacrylamide was added and the resulting solution was cooled to -78°C with a dry ice/isopropanol slurry. To the solution 1-5% initiator was added by syringe and aliquots were taken from the reaction flask to monitor the course of the reaction with time. The reaction was quenched by the addition of methanol and the solution was dripped into rapidly-stirred hexane. The specifics of each initiating system are discussed below.

n-Butyl lithium. Initiator used was in the form of a 1.6 M solution in hexane. Ten minutes after the initiator was added polymers could be precipitated by dripping into hexane. This polymer was found to be insoluble in all common organic solvents at room temperature and with prolonged heating at 60°. Immediate work-up of the remaining solution and analysis by pmr indicated that debromination of the aromatic ring had occurred.

Potassium t-butoxide. The white solid initiator was dissolved in 2 ml dry tetrahydrofuran before addition to the reaction flask. No reaction was observed when the reaction was carried out at -78°. Warming the flask to room temperature, however, and work-up of the solution after 15 minutes indicated that debromination of the aromatic ring was occurring.

Conformational Analysis

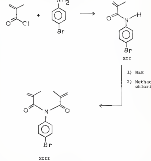
The PCILO program used was obtained from the Quantum Chemistry Program Exchange, QCPE Program No. 220/221, Chemistry Department, Indiana University. The calculations were performed on an Amdahl 470 V6 computer.

CHAPTER III
SOLID STATE INVESTIGATION

Results

Synthesis and Polymerization

The monomer, N-(p-bromophenyl)dimethacrylamide, was synthesized by the method outlined in Scheme I.



Scheme I

Methacryloyl chloride reacted with p-bromoaniline to give N-(p-bromophenyl)methacrylamide (XII) in good yield. After forming the sodium salt of (XII) long reaction times were required for the reaction with the second mole of methacryloyl chloride to form the desired N-(p-bromophenyl)dimethacrylamide (XIII) in 30% yield. Presumably the amide anion formed was stabilized enough by the electron-withdrawing effect of the para bromine substituent that longer reaction times were necessary to obtain even a low yield.

The solid state polymerization was initiated by irradiation of the crystalline monomer under vacuum with γ-rays from a cobalt-60 source and then allowing the polymerization to continue after irradiation for a period of time. The polymerization was attempted under two sets of conditions, the details of which are summarized in Table 4.

Since no polymer was isolated from the polymerization initiated at -196° only the results of the room temperature irradiation could be investigated further. The infrared spectrum of the polymer obtained is given in Figure 1. There were no detectable absorptions for alkane-H stretching and bending vibrations, indicating little or no detectable unsaturation. The 60 MHz pmr spectrum of the polymer is given in Figure 2. Again, there were no indications of residual unsaturation. In order to increase the resolution of the spectrum, the pmr of the solid state polymer was run at a higher frequency and at elevated temperatures which should help to minimize the conformational broadening of

Table 4

Solid State Polymerizations of N-(p-Bromophenyl)dimethacrylamide by γ-Irradiation

Parameter	Data[a]	
	(1)	(2)
Irradiation temperature (°C)	ambient[b]	-196
Total radiation (Mrad)	129.9	2
Post-polymerization temperature (°C)	ambient[b]	ambient[b]
Length of post-polymerization (days)	6	30
Conversion (%)	16.1	<2[c]
Solubility	acetone, $CHCl_3$, C_6H_6	--
Degree of Polymerization[d]	11 - 12	--

[a] Monomer in sealed Pyrex tubes evacuated to 10^{-5} mm.

[b] Ambient temperature was at least 80° below melting point of the monomer.

[c] Estimated from peaks in pmr of recovered monomer.

[d] Determined by gel permeation chromatography.

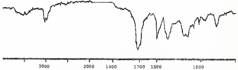


Figure 1: Infrared Spectrum (KBr) of Poly[N-(p-bromophenyl)dimethacrylamide] Obtained from Solid State γ-Irradiation

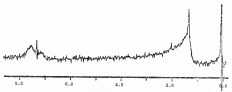


Figure 2: The PMR (60 MHz) of the Solid State Polymer of N-(p-Bromophenyl)dimethacrylamide. Spectrum was run at ambient temperatures ($CDCl_3$ solvent)

the signals. The high-field region of the spectrum obtained is given in Figure 3. Increasing the frequency of the spectrometer to 270 MHz did not appreciably resolve the peaks in the upfield region. The addition of the lanthanide shift reagent $Eu(fod)_3$ served only to further complicate the spectrum by shifting the methyl signals downfield and obliterating the methylene resonances.

Initiation of the crystalline monomer was attempted using monochromatic ultraviolet radiation. As described previously, the wavelength of maximum absorption of the monomer was found to be 220 nm. Irradiation of the monomer at that wavelength for 40 hours at room temperature resulted in no detectable polymerization. The pmr of the recovered white powder revealed only starting material. This failure to polymerize could be explained in two ways: either (1) the polycrystalline sample scattered the ultraviolet light so much that enough light was not absorbed to initiate polymerization or (2) the wavelength of maximum absorption was not the one that should be effective in initiating the polymerization reaction. Although not attempted in this study, it should be possible to differentiate between these two explanations by irradiation of a single crystal of the monomer. If the failure to polymerize was due to scatter of the incident light, the irradiation of a single crystal should result in the formation of polymer, particularly when the crystal is sufficiently thin that exposure to the light would be reasonably uniform throughout the sample.

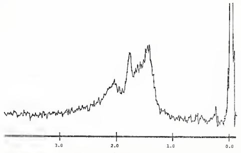


Figure 3: The PMR (100 MHz) of the Solid State Polymer of N-(p-Bromophenyl)-dimethacrylamide. Spectrum was run in nitrobenzene at 145°C

X-Ray Diffraction Study

One of the major objectives of this study was the correlation of the polymerization behavior of N-(p-bromophenyl)dimethacrylamide to its conformation in the crystal lattice. One of the most unequivocable, practical methods of determining the solid state conformation of a molecule is by small-angle X-ray diffraction. It was therefore decided that this method would be the most valuable probe for the monomer study.

After recrystallizing the monomer to obtain a single crystal suitable for analysis, geometric data collection with Weissenberg and precession cameras revealed that the monomer crystallized in an orthorhombic space group of Pbca. A drawing illustrating the atomic numbering used in the X-ray analysis is given in Figure 4. Intensity data collection and subsequent data reduction resulted in the solution of the monomer's crystal structure with a reliability index of 0.058. The computer-generated ORTEP drawing for the non-hydrogen atoms is given in Figure 5. The final positional and thermal parameters for the non-hydrogen atoms are given in Tables 5 and 6; the positional and thermal parameters for the hydrogen atoms are given in Table 7. Bond distances and angles are listed in Tables 8 and 9, respectively. Selected dihedral angles are given in Table 10. The observed and calculated structure factors appear in Appendix I.

Correlations to the polymerization behavior in the crystal lattice must, however, be made from consideration of

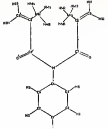


Figure 4: Numbering Scheme Used in the X-Ray Analysis of N-(p-Bromophenyl)dimethacrylamide

more than a single molecule's position. In attempting to determine the probable direction of the chain propagation it was, therefore, necessary to examine the intermolecular orientations of the reacting double bonds. The initial concern was that of the packing of the molecule in the unit cell in the eight symmetry-related positions. The computer-generated packing diagram of the unit cell is reproduced in Figure 6. Since no unit cell is isolated, it is reasonable to assume that the orientations of molecules in adjacent unit cells also play a crucial role in the polymerization

Figure 5

An ORTEP Drawing of N-(p-Bromophenyl)dimethacrylamide
Showing the Atomic Numbering and Thermal Ellipsoids

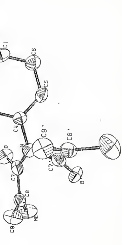

BR
C1
C2
C6
C5
C3
C4
C9'
C8'
N
O
C7
C7'
ME'
O'
C8
ME
C9

Table 5

Final Positional Parameters and their Estimated Standard Deviations for N-(p-Bromophenyl)dimethacrylamide

Atom[a]	x	y	z
C9'	3752 (3)	7028 (10)	4906 (9)
C8'	3452 (3)	6577 (10)	5724 (8)
C7'	3316 (3)	4874 (10)	5784 (8)
O'	2936 (2)	4492 (7)	6017 (5)
N	3658 (2)	3756 (7)	5506 (6)
C7	3522 (2)	2317 (11)	4995 (8)
O	3727 (2)	1126 (6)	5258 (6)
C8	3155 (2)	2362 (11)	4069 (8)
C9	3162 (3)	3432 (12)	3180 (9)
Me'	3168 (4)	7642 (13)	6548 (10)
Me	2825 (3)	1112 (12)	4168 (10)
C4	4084 (2)	3892 (9)	6129 (8)
C3	4473 (3)	3480 (10)	5477 (8)
C2	4886 (2)	3590 (10)	6070 (9)
C1	4910 (2)	4111 (10)	7272 (8)
C6	4522 (2)	4553 (10)	7927 (8)
C5	4107 (2)	4422 (11)	7334 (7)
Br	5471 (0)	4334 (2)	8067 (1)

[a] Values for all atoms times 10^4

Table 6

Final Thermal Parameters and Their Estimated Standard Deviations for N-(p-Bromophenyl)dimethacrylamide

Atom[a]	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
C9'	13 (12)	117 (18)	98 (11)	-12 (8)	2 (6)	24 (25)
C8'	12 (12)	87 (14)	76 (10)	19 (7)	-18 (6)	-42 (23)
C7'	10 (1)	93 (15)	57 (9)	14 (7)	-8 (5)	1 (21)
O'	7 (1)	110 (10)	104 (7)	7 (5)	4 (3)	-3 (17)
N	8 (1)	58 (10)	72 (7)	-6 (5)	-1 (4)	-33 (16)
C7	9 (1)	93 (14)	69 (8)	-14 (7)	12 (5)	-33 (23)
O	12 (1)	61 (8)	132 (8)	-1 (5)	-8 (4)	-20 (15)
C8	8 (1)	104 (14)	72 (9)	-3 (8)	1 (5)	-72 (24)
C9	14 (1)	177 (19)	71 (10)	-7 (8)	-13 (7)	23 (27)
Me'	26 (2)	86 (16)	135 (14)	-8 (11)	10 (9)	-50 (28)
Me	15 (1)	144 (19)	154 (15)	-39 (9)	-37 (8)	-2 (31)
C4	7 (1)	63 (13)	71 (9)	-4 (6)	-6 (5)	6 (19)
C3	8 (1)	107 (14)	68 (9)	0 (7)	2 (5)	-7 (21)
C2	7 (1)	107 (15)	98 (11)	-8 (7)	7 (6)	2 (24)
C1	8 (1)	92 (16)	106 (12)	-11 (7)	-17 (5)	36 (23)
C6	8 (1)	134 (15)	77 (8)	8 (8)	-10 (6)	7 (24)
C5	8 (1)	123 (15)	66 (9)	0 (8)	8 (4)	13 (23)
Br	9 (0)	302 (2)	148 (1)	6 (1)	-28 (1)	-59 (4)

[a] Values for all atoms times 10^4.

Table 7

Final Positional and Isotropic Thermal Parameters and Estimated Standard Deviations for Hydrogen Atoms of N-(p-Bromophenyl)dimethacrylamide

Atom 1	Bonded to Atom 2	x^a	y^a	z^a	B
H2	C2	5145(26)	3376 (98)	5634 (74)	5.8(2.3)
H3	C3	4426(18)	3341 (69)	4630 (54)	1.6(1.4)
H5	C5	3842(18)	4606 (72)	7769 (54)	1.6(1.4)
H6	C6	4532(23)	5041 (81)	8903 (66)	3.9(1.8)
H91	C9	2900(21)	3391 (76)	2556 (64)	3.2(1.7)
H92	C9	3418(23)	3802 (87)	3096 (74)	4.7(2.0)
H93	C9'	3859(23)	7921 (89)	4710 (71)	4.8(2.1)
H94	C9'	3911(30)	6344(108)	4074 (87)	8.1(2.8)
HM1	Me	2704(30)	685(123)	3526 (90)	10.0(3.0)
HM2	Me	2579(39)	1310(132)	3570(103)	12.1(3.8)
HM3	Me	2918(22)	421 (92)	4144 (67)	4.0(1.9)
HM4	Me'	3038(35)	7144(151)	7516(112)	14.3(3.7)
HM5	Me'	3292(24)	8233 (88)	6540 (70)	3.8(2.1)
HM6	Me'	3362(33)	7488(154)	7261(104)	12.7(3.3)

[a] Values for all positional parameters times 10^4.

Table 8

Bond Distances (Å) with their Estimated Standard Deviations for N-(p-Bromophenyl)dimethacrylamide

Atoms	Distance	Atoms	Distance
Br-C1	1.883 (8)	C2-H2	0.919 (79)
C1-C2	1.374 (13)	C3-H3	0.932 (58)
C2-C3	1.388 (11)	C5-H5	0.931 (55)
C3-C4	1.400 (11)	C6-H6	1.133 (71)
C4-C5	1.380 (12)	C9-H91	1.030 (66)
C5-C6	1.393 (11)	C9-H92	0.830 (71)
C6-C1	1.407 (11)	Me-HM1	0.862 (98)
C4-N	1.439 (10)	Me-HM2	0.990 (114)
N-C7	1.409 (11)	Me-HM3	0.653 (77)
C7-O	1.222 (10)	C9'-H93	0.856 (76)
C7-C8	1.479 (11)	C9'-H94	1.172 (93)
C8-C9	1.327 (13)	Me'-HM4	1.193 (121)
C8-Me	1.456 (13)	Me'-HM5	0.624 (75)
N-C7'	1.428 (10)	Me'-HM6	0.970 (108)
C7'-O'	1.203 (9)		
C7'-C8'	1.514 (12)		
C8'-C9'	1.312 (13)		
C8'-Me'	1.527 (14)		

Table 9

Bond Angles (°) with their Estimated Standard Deviations for N-(p-Bromophenyl)dimethacrylamide

Atoms	Angle	Atoms	Angle
Br-C1-C2	120.6(0.6)	Me'-C8'-C9'	126.2(0.8)
C1-C2-C3	120.2(0.8)	C1-C2-H2	120.3(5.1)
C2-C3-C4	118.9(0.8)	H2-C2-C3	119.3(5.1)
C3-C4-C5	121.0(0.7)	C2-C3-H3	126.4(3.6)
C4-C5-C6	120.3(0.8)	H3-C3-C4	113.6(3.6)
C5-C6-C1	118.3(0.8)	C4-C5-H5	119.3(3.6)
C6-C1-C2	121.3(0.8)	H5-C5-C6	120.2(3.6)
Br-C1-C6	118.1(0.6)	C5-C6-H6	118.8(3.6)
C3-C4-N	118.3(0.7)	H6-C6-C1	122.9(3.6)
C5-C4-N	120.8(0.7)	C8-C9-H91	115.9(3.8)
C4-N-C7	120.4(0.6)	H91-C9-H92	129.5(6.4)
C7-N-C7'	118.3(0.6)	C8-C9-H92	110.9(5.2)
C4-N-C7'	117.6(0.6)	C8-Me-HM1	122.2(6.6)
N-C7-O	119.7(0.7)	C8-Me-HM2	108.8(6.6)
N-C7-C8	117.0(0.7)	C8-Me-HM3	112.3(6.5)
O-C7-C8	123.1(0.8)	HM1-Me-HM2	40.6(9.2)
C7-C8-C9	119.6(0.8)	HM1-Me-HM3	76.0(9.1)
C7-C8-Me	115.3(0.8)	HM2-Me-HM3	116.1(9.2)
Me-C8-C9	124.9(0.8)	C8'-C9'-H93	133.1(5.0)
N-C7'-O'	122.0(0.7)	H93-C9'-H94	96.1(6.7)
N-C7'-C8'	116.5(0.7)	C8'-C9'-H94	130.0(4.6)
O'-C7'-C8'	121.4(0.7)	C8'-Me'-HM4	118.4(5.8)
C7'-C8'-C9'	119.5(0.8)	C8'-Me'-HM5	98.7(6.9)
C7'-C8'-Me'	113.7(0.8)	C8'-Me'-HM6	93.1(6.8)

continued

Table 9 (continued)

Atoms	Angle
HM4-Me'-HM5	119.5(9.0)
HM4-Me'-HM6	56.6(8.9)
HM5-Me'-HM6	76.9(9.6)

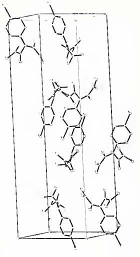
Table 10

Selected Dihedral Angles (°) for
N-(p-Bromophenyl)dimethacrylamide

Atoms	Angle	Atoms	Angle
C9'-C8'-C7'-N	33.68	C7'-C8'-C9'-H93	1.69
C8'-C7'-N-C7	208.81	C7'-C8'-C9'-H94	181.03
C7'-N-C7-C8	39.58	C9'-C8'-Me'-HM4	43.94
N-C7-C8-C9	44.34	C9'-C8'-Me'-HM5	160.71
C9'-C8'-C7'-(Me')	189.02	C9'-C8'-Me'-HM6	288.41
C9'-C8'-C7'-O'	215.93	C7-C8-C9-H91	1.85
C7'-N-C7-O	213.98	C7-C8-C9-H92	177.50
N-C7-C8-Me	220.30	C7-C8-Me-HM1	123.47
C8'-C7'-N-C4	50.24	C7-C8-Me HM2	2.63
C7'-N-C4-C3	325.45	C7-C8-Me-HM3	245.86
N-C4-C3-C2	180.69	N-C4-C3-H3	347.64
C4-C3-C2-C1	0.68	C4-C3-C2-H2	185.11
C7'-N-C4-C5	145.87	N-C4-C5-H5	2.43
N-C4-C5-C6	179.80	C4-C5-C6-H6	168.92
C3-C2-C1-Br	177.63		

Figure 6

A Packing Diagram of the Unit Cell of N-(p-Bromophenyl)dimethacrylamide
Showing the Eight Symmetry-related Positions



process. Considering a unit cell, the symmetry related positions of monomers in unit cells directly above, below and to either side of half of that unit cell were, therefore, plotted and are reproduced in Figure 7. From these symmetry related monomers the intramolecular and intermolecular distances and their estimated standard deviations for the atoms involved in the polymerization process (C8, C9, C8', and C9') were calculated and are summarized in Tables 11, 12, 13, and 14.

Electron Spin Resonance

An investigation into the nature of the propagating species was made through the use of esr techniques. Irradiation of the monomer with γ-rays was carried out at -196°C and the sample was allowed to warm to room temperature. The esr spectrum of the polycrystalline sample run one day after the irradiation is given in Figure 8a. Computer simulation nearly reproduced the spectrum when it was estimated that the radical was interacting with three equivalent and two non-equivalent hydrogens with the following hyperfine coupling constants: $a_{\beta}CH_3$ = 20 gauss; $a_{\beta}CH$ = 9 gauss, and $a_{\beta}CH$ = 35 gauss. The intensities of the fifth, sixth, and ninth lines from the left of the spectrum were, however, never quite reproduced in the simulation. One very plausible explanation for this irreproducibility centered on the likelihood of more than one radical species contributing to the spectrum. It was decided that more information concerning the formation of these several species could be obtained from the esr

Figure 7

A Packing Diagram of the Unit Cell of N-(p-Bromophenyl)dimethacrylamide With Monomers Above, Below, and to Either Side of the Unit Cell

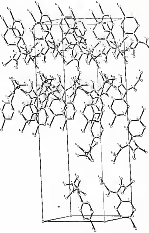


Table 11

Intra- and Intermolecular Distances and Their Estimated Standard Deviations in the Crystal Lattice from C8 (Atom 1)

Atom 2	Symmetry Relation between A_1 and A_2	Distance (Å)
C8'	*Intramolecular	4.122 (0.012)
C9'	*Intramolecular	4.463 (0.012)
C9	$x, \frac{1}{2} - y, \frac{1}{2} + z$	4.489 (0.013)
C9'	$x, y-1, z$	4.981 (0.012)
C9'	$\frac{1}{2} - x, -[\frac{1}{2} - y], z$	5.746 (0.011)
C9'	$x, \frac{1}{2} - y, -(\frac{1}{2} - z)$	6.119 (0.013)
C8'	$x, y-1, z$	5.338 (0.013)
C8'	$\frac{1}{2} - x, -[\frac{1}{2} - y], z$	5.143 (0.011)
C8'	$x, \frac{1}{2} - y, -(\frac{1}{2} - z)$	6.382 (0.012)
C8'	$x, \frac{1}{2} - y, -[\frac{1}{2} - z]$	5.018 (0.012)
C8'	$\frac{1}{2} - x, 1-y, -(\frac{1}{2} - z)$	6.055 (0.011)
C8	$x, \frac{1}{2} - y, \frac{1}{2} + z$	5.401 (0.012)
C9	$\frac{1}{2} - x, -(\frac{1}{2} - y), z$	5.250 (0.012)
C8	$\frac{1}{2} - x, -[\frac{1}{2} - y], z$	5.787 (0.012)

Table 12

Intra- and Intermolecular Distances and their Estimated Standard Deviations in the Crystal Lattice from C9 (Atom 1)

Atom 2	Symmetry Relation between A_1 and A_2	Distance
C8'	*Intramolecular	3.940 (0.013)
C9'	*Intramolecular	4.002 (0.013)
C8	$x, \frac{1}{2} - y, (\frac{1}{2} + z)-1$	4.489 (0.013)
C9'	$x, y-1, z$	6.050 (0.013)
C9	$\frac{1}{2} - x, \frac{1}{2} + y, z$	5.815 (0.013)
C9	$\frac{1}{2} - x, -(\frac{1}{2} - y), z$	5.815 (0.013)
C9	$x, \frac{1}{2} - y, \frac{1}{2} + z$	5.627 (0.014)
C9	$x, \frac{1}{2} - y, -(\frac{1}{2} - z)$	5.627 (0.014)
C9'	$x, y - 1, z$	6.050 (0.013)
C9'	$\frac{1}{2} - x, -(\frac{1}{2} - y), z$	6.105 (0.012)
C9'	$x, \frac{1}{2} - y, -(\frac{1}{2} - z)$	5.537 (0.013)
C9'	$x, \frac{1}{2} - y, -(\frac{1}{2} - z)$	6.116 (0.013)
C8'	$\frac{1}{2} - x, -(\frac{1}{2} - y), z$	5.751 (0.012)
C8'	$x, 1 + (\frac{1}{2} - y), -(\frac{1}{2} - z)$	5.100 (0.013)

Table 13

Intra- and Intermolecular Distances and their Estimated Deviations in the Crystal Lattice from C8' (Atom 1)

Atom 2	Symmetry Relation between A_1 and A_2	Distance (Å)
C8	*Intramolecular	4.122 (0.012)
C9	*Intramolecular	3.940 (0.013)
C9'	$x, \frac{1}{2} - y, \frac{1}{2} + z$	4.753 (0.013)
C9'	$x, \frac{1}{2} - y, (\frac{1}{2} + z) - 1$	6.453 (0.013)
C8	$x, 1 + y, z$	5.338 (0.013)
C8	$\frac{1}{2} - x, \frac{1}{2} + y, z$	5.143 (0.011)
C9	$\frac{1}{2} - x, \frac{1}{2} + y, z$	5.751 (0.012)
C8'	$x, \frac{1}{2} - y, -[\frac{1}{2} - z]$	5.623 (0.012)
C8	$x, 1 + (\frac{1}{2} - y), \frac{1}{2} + z$	6.382 (0.012)
C9	$x, 1 + (\frac{1}{2} - y), \frac{1}{2} + z$	5.101 (0.013)
C8'	$x, \frac{1}{2} - y, \frac{1}{2} + z$	5.623 (0.012)
C8	$x, \frac{1}{2} - y, \frac{1}{2} + z$	5.018 (0.012)
C9	$x, \frac{1}{2} - y, \frac{1}{2} + z$	5.115 (0.013)
C8	$\frac{1}{2} - x, -y, \frac{1}{2} + z$	6 055 (0 011)

Table 14

Intra- and Intermolecular Distances and their Estimated Standard Deviations in the Crystal Lattice from C9'
(Atom 1)

Atom (2)	Symmetry Relation between A_1 and A_2	Distance (Å)
C9	*Intramolecular	4.002 (0.013)
C8	*Intramolecular	4.463 (0.012)
C8'	$x, \frac{1}{2} - y, \frac{1}{2} + z$	4.753 (0.013)
C8	$x, 1 + y, z$	4.981 (0.012)
C9'	$x, \frac{1}{2} - y, -(\frac{1}{2} - z)$	5.456 (0.014)
C8'	$x, \frac{1}{2} - y, \frac{1}{2} + z$	6.453 (0.013)
C9	$x, 1 + (\frac{1}{2} - y), \frac{1}{2} + z$	5.537 (0.013)
C8	$x, -(\frac{1}{2} + y), \frac{1}{2} + z$	6.119 (0.013)
C9	$x, \frac{1}{2} - y, \frac{1}{2} + z$	6.116 (0.013)
C9	$x, 1 + y, z$	6.050 (0.013)
C8	$\frac{1}{2} - x, \frac{1}{2} + y, z$	5.746 (0.011)
C9	$\frac{1}{2} - x, \frac{1}{2} + y, z$	6.105 (0.012)
C8	$x, \frac{1}{2} - y, \frac{1}{2} + z$	5.456 (0.014)

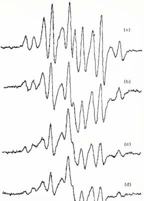


Figure 8: The ESR Spectra of γ-Irradiated N-(p-Bromophenyl)-dimethacrylamide (a) 1 Day, (b) 1 Week, (c) 1 Month after Irradiation; (d) 4 Days after Opening to Air

measurements on an irradiated single crystal at various temperatures between and including -196°C and 20°C. Research in this direction is currently in progress.

Similar esr measurements were made over the next month on the same polycrystalline sample (Figure 8b and 8c). Although they were generally characterized by some loss of fine structure and intensity, there still remained a fairly large amount of radical centers in the sample over a long period of time. Exposure of the sample to air for four days did not appreciably affect the spectrum, as shown in Figure 8d. This was consistent with the probable slow diffusion of oxygen through the crystal lattice.

Discussion

The field of solid state polymerization apparently held little attraction for polymer chemists until the early 1950s. Unlike liquid monomers which often polymerize on standing unless inhibited, crystalline vinyl and vinylidene compounds were known to be quite stable for long periods of time. Though reports were published before World War II on the polymerization of liquid monomers with γ-rays[57, 58, 59] the experiments were not extended to the crystalline phase until 1951.[60] The systematic investigation of the processes that were occurring in the solid state polymerizations really only began in 1954.[61, 62] The possibility of these polymerization processes being highly oriented and therefore leading to the formation of crystalline, oriented polymers spurred research efforts in the late fifties and the sixties, and it was found that these polymerizations could be initiated by X-rays and electron beams as well.

The first example of cyclopolymerization in the solid state was reported by Gibbs and Van Deusen[63] in 1961. It was found that when N,N-diallylmelamine was irradiated with γ-rays from a cobalt-60 source a linear soluble polymer was obtained which contained no detectable unsaturation. It was, therefore, concluded that cyclopolymerization had been induced in the solid state.

Solid state investigation of the polymerization behavior of dimethacrylamides was first begun by M. Azori et al.[64] in 1966, with their report of the effect of X-ray irradiation on crystals of N-phenyldimethacrylamide. In 1971, Butler and Myers reported the γ-ray initiation of solid state polymerizations of dimethacrylamide and its N-methyl and N-phenyl derivatives.[40] Both studies reported the formation of linear soluble polymers with exposure to the ionizing radiation. A comparison of the results reported for N-phenyldimethacrylamide, the unbrominated precursor for this study, is given in Table 15.

There are two primary methods of carrying out the polymerization of a crystalline monomer by exposing the crystals to the radiation at the polymerization temperature or by polymerizing at a suitable temperature crystals that were preirradiated at a much lower temperature at which chain propagation is presumably insignificant. Generally, of these two, the latter process is preferred because the processes

Table 15

Results of Previous Solid State Polymerizations of N-Phenyldimethacrylamide

Parameter	Data[a]	Data[b]
Radiation type	X-ray	γ-ray
Irradiation temperature	75°[c]	Ambient
Dose rate (Mrad/hr)	0.2	0.5 1.4
Irradiation time (hrs)	1.67 5	26 65
Total dose (Mrad)	0.34 1.0	13 91
Conversion (%)	10 60	-- 22
Intrinsic viscosity	0.26 0.16	-- 0.06

[a] M. Azori, N.A. Plate, G.D. Rudkovskaya, T.A. Sokolova, and V.A. Kargin, Vysokomolekul. Soedin., 8, 759 (1966).

[b] G.B. Butler and G.R. Myers, J. Macromol. Chem., A5(1), 135 (1971).

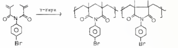
[c] Temperature in °C is 5° below the melting point.

are better controlled and it avoids the exposure of the macromolecules to the radiation. Thermal control of the exothermic polymerization may also be somewhat better maintained by the latter procedure.

In this study the polymerization of N-(p-bromophenyl)-dimethacrylamide was attempted by both procedures. The results are summarized in Table 4. When the irradiation was performed at -196° and the post-polymerization effected at ambient temperatures for 30 days, essentially no polymer was obtained. However, when the irradiation was performed at ambient temperatures at a much larger dose, post-polymerization of 6 days yielded a 16% conversion to soluble polymer. Since the polymer obtained was soluble in several common organic solvents it was concluded that crosslinking or branching had not occurred to an appreciable extent during the irradiation.

There are at least two possible ways in which the yield from the low temperature irradiations could have been improved: (1) by increasing the total dose to the sample, and (2) by increasing the temperature at which post-polymerization was effected. In the first case, a phenyl ring in the monomer molecule has a strong tendency to absorb the energy from the ionizing radiation and then dissipate it thermally. This proposal is supported by the data reported by Butler and Myers[40] in which lower total doses were required to polymerize N-methyldimethacrylamide than N-phenyldimethacrylamide. Conceivably, then, a total dose of 2 Mrad was not enough to initiate appreciable polymerization even though esr measurements on a sample that had been similarly irradiated indicated that an appreciable amount of radical centers had been generated. In the second case, the possibility of zone melting occurring at the polymer interphase exists, and, therefore, the polymers may be formed more as a result of a liquid rather than solid state process. Quite likely, the large yields obtained by M. Asori et al.[64] were results of exactly these same phase transitions and were not true solid state processes at all.

Since the polymer obtained from the solid state irradiation was soluble in common organic solvents and both infrared and pmr spectra indicated no residual unsaturation it was presumed that polymerization had occurred by an alternating intramolecular-intermolecular reaction. The polymer backbone could be composed of five- or six-membered rings or both as shown by the following equation. To distinguish between



these two possibilities the infrared spectrum of the polymer was first examined. The carbonyl stretching frequencies of cyclic imides are very sensitive to the ring size with imides of a five-membered ring generally absorbing at a higher frequency than those in a six-membered ring. In 1967, Sokolova and Rudkovskaya[9] reported the infrared spectra of the polymers obtained by the deamination of poly-(N-substituted methacrylamide) where the N-substituent was methyl, ethyl, propyl, and phenyl. The spectra of these polymers were also compared with those of the appropriate N-substituted succinimides and glutarimides. The results of their study when the N-substituent was phenyl are summarized in Table 16.

Examination of the 1600-1800 cm^{-1} range in the infrared spectrum of poly[N-(p-bromophenyl)dimethacrylamide] in Figure 1 revealed a strong absorption at 1710 cm^{-1} and shoulders at approximately 1780, 1680, and 1730 cm^{-1}. Since the first two absorptions correlated well with the carbonyl stretch of six-membered cyclic imides [N-phenylglutarimide and the polymer resulting from the deamination of poly(N-phenylmethacrylamide)] and the second two with those of the five-membered cyclic imide, N-phenylsuccinimide, it was concluded that the infrared analysis afforded strong evidence for the existence of both five- and six-membered rings in poly[N-(p-bromophenyl)dimethacrylamide]. The exact percentages of each, however, could not be determined using the infrared spectrum.

The high field region of the high resolution pmr spectrum of the solid state polymer contained two resonances at $\delta 1.47$ and $\delta 1.71$ which correspond to the chemical shifts reported for the methyl hydrogens on a five- and six-membered cyclic imide ring, respectively.[40] The two peaks were very broad, however, and overlap which made quantitative assessment of the structure approximate at best.

Table 16

Infrared Carbonyl Stretching Frequencies of N-Phenyl Polyimides and Cyclic Imides

Compound Type	R	C=O $(cm^{-1})^a$	
		1	2
	C_6H_5	1678	1730
	C_6H_5	1712	1780
Deamination of 	C_6H_5	1680	1730
Free Radical Polymer of 	C_6H_5	1715	1787

[a] T.A. Sokolova and G.D. Rudkovskaya, J. Polym. Sci., C, 1157 (1967).

It was determined that carbon-13 nmr would not be of practical value in this particular structure determination because of the possibility of forming different stereoisomers at every ring juncture. With two optically active sites potentially forming in every ring and the ring either consisting of five or six members, the polymer could have a very large number of stereoisomers available to it even if there was a low degree of polymerization. Synthesis and isolation of model compounds with proper stereoisomerism alone could involve more work than the information merited. An added difficulty in the use of the carbon-13 analysis for quantitative work would involve the necessary minimization of the Nuclear Overhauser Effect.

In summarizing, all available spectral tools indicated that the monomer, N-(p-bromophenyl)dimethacrylamide, had polymerized to a linear soluble polymer with no detectable residual unsaturation. Very rough estimation of the resonances observed in the 100 MHz pmr spectrum indicated a mixture of possibly as much as 60% five-membered rings and 40% six-membered rings.

The processes by which the polymer was formed were even more difficult to elucidate than the structure. Considering the rigid orientation of the monomer molecules in the crystal lattice, it is somewhat surprising that these processes occur at all. While diffusion of reacting species towards each other can occur readily in the liquid or gaseous state, it is much more difficult in the solid phase where molecular mobility is limited by lattice restraints. Since this diffusion is a prerequisite for all chemical reactions, motion of some type must nevertheless occur after initiation by irradiation for the reaction to propagate. The feasibility of solid state processes should, therefore, hinge more on the spatial relationships of the reactive groups in the crystal lattice than on their chemical reactivity. Indeed, monomers with vinyl groups of very similar intrinsic reactivity often differ widely in their mode of reaction in the crystalline state. There exist in the literature many indications that the geometry of the lattice does exhibit control on whether or not a reaction will occur and, if so, which direction it will take.[65-69]

One considerable difficulty in the study of solid state processes lies in determining whether the observed reaction is actually a result of the solid rather than the liquid phase processes. This should be of concern in this study since the monomer (as well as many other organic molecules) had a relatively low melting point. In vinyl monomers the polymerization process involves the breaking of a double bond and the subsequent formation of a new carbon-carbon bond, the overall process leading to a pronounced contraction with an energy release of approximately 10 to 15 kcal/mole. Such a large energy release could result in partial melting of the crystal at the polymerization site. In these cases convincing criteria are necessary to indicate that the reaction observed is determined by the geometrical arrangement of the molecules in the crystal and is not a result of that partial liquid phase. Some of the following types of evidence[70] are valuable in establishing that the crystal lattice controls the course of the reaction:

(1) The crystalline phase of the molecule may react while the liquid state does not react or reacts at a much slower rate.

(2) Closely related compounds react very differently in the solid phase.

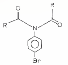
(3) Different reaction products are obtained from the solid state reaction than from the solution reaction.

(4) Different crystal modifications of a compound result in different reactivity or different reaction products.

(5) Products are formed that are oriented in a specific crystallographic direction of the parent molecule.

In an attempt to determine how the cyclopolymer of N-(p-bromophenyl)dimethacrylamide was formed and what role the crystal lattice played, an X-ray diffraction study of the monomer was undertaken. Once the exact positions of the atoms were known, it might be easier to determine why the polymer formed as it did.

An initial inspection of the ORTEP drawing in Figure 5 led to several interesting observations. First, the imide was roughly in a trans-cis orientation as shown below. This correlated well with the early predictions[42] that dimethacrylamides would be conformationally similar to diacetamide and N-methyldiacetamide. However, there was



not a coplanar arrangement of the imide group which was predicted to allow maximum delocalization of the pi clouds. Dihedral angle measurements indicated that O' was skewed out of the plane containing C7'-N-C7 by 26.6° while O was skewed out by 34.18°. The phenyl ring oriented in a plane with a dihedral angle of 65° to the imide plane and therefore extended conjugation of the imide group through the phenyl ring would be very unlikely.

Equally striking, albeit somewhat expected, was the observation that neither of the methacryl groups had a coplanar arrangement of the carbon-carbon double bond and the carbonyl group in the crystalline state. There was a dihedral angle of 215.9° between the atoms C9'-C8'-C7'-O', which was nearly 36° away from a coplanar arrangement. Similarly, the atoms O-C7-C8-C9 oriented with a dihedral angle of 230.16° which was roughly 50° from a coplanar arrangement.

Though both groups were in the s-trans orientation, the molecule had crystallized in a conformation that did not allow maximum overlap of the pi clouds, presumably in a higher energy orientation.

Perhaps the most interesting aspect of the monomer conformation (and certainly the most relevant to the polymerization process) was the relative orientation of the two double bonds with respect to each other. The plane containing C9'-C8'-Me' and that containing C9-C8-Me were at an angle of 87.45° to each other. This nearly perpendicular arrangement of the two double bonds would almost certainly allow no possibility for a through-space overlap of the pi clouds of the two carbon-carbon double bonds. Therefore, it was immediately obvious that the monomer did not crystallize in a conformation that would favor the proposed[30] through-space nonconjugated interaction of the double bonds.

If the cyclopolymerization could not be explained on the basis of a preorientation from a nonconjugated interaction, how, then, did the polymerization processes occur? Why did irradiation of the monomer lead exclusively to cyclopolymer? A comparison of the intramolecular and intermolecular distances between the carbon atoms involved in the polymerization reactions uncovered a consistent trend that could shed light on these questions. However, in order that such a comparison might be fully appreciated, it might be appropriate to first mention a systematic study performed by Schmidt and coworkers on the relationship between lattice geometry and the photodimerization of olefins.[71-73] Their experiments showed that the photolysis product distribution could be explained by correlation to the corresponding crystal structure of the reacting molecules. For trans-cinnamic acid, the "α-type" (with an antiparallel packing of adjacent molecules and 3.7 Å between the nearest neighbors) led exclusively to the formation of head-t -tail dimer upon photolysis. On the other hand, the "β-type" in which the adjacent molecules were parallel with 4.0 Å between the nearest neighbors led, upon photolysis, exclusively to head-to-head dimer. When the nearest neighbors were never less than 4.7 Å apart and adjacent molecules were antiparallel as in the "γ-type" direct photolysis yielded no dimerization. A general rule that derived from these and similar data was that photodimerization occurred only in those crystals in which the distance between the adjacent double bonds was less than the critical value of 4 Å. For longer distances the compound was light stable. Hirshfeld and Schmidt[74] extended that postulate to compounds that undergo solid state polymerization for which crystallographic data were available. Their survey once again supported the postulate that the polymerization reaction would be possible only if the monomer's crystal structure afforded such close contact between the reacting centers.

These data and the resulting hypothesis were valuable in explaining the solid state polymerization behavior of N-(p-bromophenyl)dimethacrylamide. Examination of the pertinent crystallographically determined intramolecular and intermolecular distances for the reacting atoms, C8, C9, C8', and C9', which are summarized in Table 17, served to clarify the processes considerably. Intramolecular

Table 17

Pertinent Intramolecular and Intermolecular Distances for Atoms Involved in the Solid State Polymerization of N-(p-Bromophenyl)dimethacrylamide

Atom	Intramolecular Reactors		Closest Intermolecular Reactor	
	Atom	Distance (Å)	Atom	Distance (Å)
C9	C8'	3.940	C8	4.489
	C9'	4.002		
C8	C8'	4.122	C9	4.489
	C9'	4.453		
C8'	C8	4.122	C9'	4.753
	C9	3.940		
C9'	C8	4.453	C8'	4.753
	C9	4.002		

distances from C9 to C8' and C9' were 3.940 Å and 4.002 Å, respectively, while the closest intermolecular reactive site was nearly an half Angstrom further away (4.489 Å to C8). The closest intramolecular route for C8 was with C8' which was 4.122 Å away. The other intramolecular site, C9' was 4.453 Å removed which was almost as far away as the nearest intermolecular site (C9 at 4.489 Å). The atom C8' was fairly close to its two possible intramolecular reactors which was C8 at 4.122 Å and C9 at 3.940 Å. The closest intermolecular reactor, C9', was 0.6 Å further away. And, finally, the closest intramolecular reacting site for C9' was C9 which was 4.002 Å away. The second intramolecular possibility, C8, was 0.4 Å further away and the nearest potential intermolecular route was even further separated - C8' at 4.753 Å. All of the carbons in the double bonds had a least one and, in some cases, two potential intramolecular reactive sites that were approximately 4 Å away, the critical distance found by Schmidt beyond which reaction should not occur. All other potential reactors (both intramolecular and intermolecular) were at least 0.4 - 0.7 Å further away.

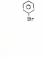
The significance of the distances separating the reacting centers might be further emphasized by pointing out exactly what type of barriers are involved for movement within the molecular crystal. The activation energies for such processes are usually quite high, a fact which is borne out by the persistence of the anisotropy of electron spin resonance spectra of irradiated single crystals such as glycine,[75] alanine,[76] and malonic acid[77] over a period of months. The radicals which were generated in the crystal remain precisely oriented in the crystal lattice, indicating a very limited extent of diffusion. The diffusion coefficient of single crystals of anthracene was estimated by tracer techniques[78] to be 1 - 2 x 10^{-10} $cm^2 sec^{-1}$ at 177°C (40°C below the melting point). This value is about five orders of magnitude below typical data for liquids. The activation energy for the diffusion of anthracene molecules in the crystal lattice was estimated as 42 kcal/mole.

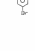
Since these diffusion processes are so slow and the activation energies so high the course of the solid state reaction should be very much determined by the distances separating the reactive sites. After irradiation with the cobalt-60 γ-rays the initiating species is formed at one of the two carbon-carbon double bonds. Once formed, whether it be an ion or radical, the species will have a different configuration than it had in the unreacted form. As these changes are unpredictable it would be impossible to determine precisely the relative orientation of the species to the other reaction sites. Since the atoms must diffuse from a distance of 4 Å apart to the distance of the carbon-carbon single bond (approximately 1.4 Å) it is also highly questionable whether their original orientation would be maintained through such a displacement. Therefore, correlations of the crystallographically determined atomic positions to the ring sizes in the polymer backbone would be somewhat unfounded. However, in all cases the distance between the shortest intramolecular route and the shortest intermolecular one (0.4 - 0.7 Å differences) was large enough that it was reasonable to predict that the initial orientation changes would not drastically change this trend. Therefore, it appeared that the molecule had crystallized out in a conformation that would favor intramolecular propagation over the intermolecular route as long as the crystal lattice maintained control on the polymerization.

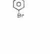
Since the intermolecular distances calculated were so large it is somewhat surprising that the molecule was capable of reacting with a second molecule at all. One contributing factor that could facilitate that propagation was the possibility that the phenyl ring dissipated thermally the radiation it absorbed. The heat released might have been enough to increase molecular vibrations until propagation could occur. Once an addition did occur the heat of polymerization released might also contribute to the molecular mobility. It should be pointed out, though, that, even with these factors, the degree of polymerization was measured to be only 11 or 12, indicating that these polymerization processes were still not extremely easy. This was almost certainly due to the large distances through which the reacting sites had to diffuse before reaction could occur.

Examination of the symmetry relations between the reacting atoms and the closest intermolecular reactors (Tables 11 - 14) revealed that the shortest distance between the carbon-carbon double bonds was always in one crystallographic direction $[x, \frac{1}{2} - y, \frac{1}{2} + z]$. Therefore, polymerization, as long as it was controlled by the geometric arrangements of the monomer molecules in the crystal lattice, should be along that one axis. However, if the crystal becomes disordered and the relative orientation of the monomer molecules in the lattice change, the polymer formed might no longer be a result of these crystallographically-determined lattice restraints. Evidence has been presented in the literature that both discounted[56, 79, 80] and supported[81] the disordering of the unreacted crystal lattice during the polymerization.

In an attempt to investigate more completely the processes occurring in the solid phase electron spin resonance studies were made on irradiated polycrystalline samples of the monomer. The spectra obtained were reproduced in Figure 8. It was immediately obvious that radical centers were generated by the radiation, although the concentration of the centers was not determined. The most probable species that could have been present in the irradiated sample are given below. Differentiation between the first two would be fairly difficult unless the coupling constants of the β-hydrogens were widely different for the two intermediates. The third, however, would be expected to give a esr spectrum consisting of a triplet with 1:2:1







intensities. Since the computer simulation did not reproduce the spectra exactly it is quite likely that at least two and possibly all three of these species were present in the sample. The slight changes in the intensities and fine structure of the spectra with time could be attributed to propagation occurring or radical recombinations and terminations. The persistence of the strong signal over such a long time was certainly indicative of the restricted mobility of the monomers in the crystal lattice. Had the temperature been higher, however, it is likely that the mobility could have been considerably increased and the reactions occurring would have been much faster. A similar study reported by Kodaira, et al.[82] on the γ-irradiation of N-methyldimethacrylamide indicated that the 12-line spectrum obtained did not change with prolonged heating of the sample at 303° K although its intensity decreased. They did not report the effect of higher temperature on the signal. Once the radical centers were generated in the crystalline monomer they apparently continued reacting at room temperature and would continue to do so until the polymerization tube was opened and the sample dissolved.

Even more information about the polymerization processes could be obtained from esr measurements on an irradiated single crystal. Since the monomer's position in the crystal lattice was determined fairly precisely as well as the crystallographic direction through which propagation should initially occur, it should be possible to monitor changes in the crystal lattice due to the polymerization processes. Generation of active centers in a single crystal by γ-irradiation at -196°C has been shown to result in the formation of radical sites that are precisely oriented with respect to the crystal axes.[70,83] Examination of the esr signal from irradiated N-(p-bromophenyl)dimethacrylamide when each of the three axes were parallel to the magnetic field of the spectrometer should, therefore, reveal an orientation effect (anisotropy) in the spectra. As the sample is warmed cyclization should occur at some temperature T_1 resulting in a new intermediate with perhaps a new orientation in the crystal lattice. A change in the anisotropy of the signal might be detectable at that temperature. As the temperature of the sample is raised even further, intermolecular propagation should occur at a temperature T_2 when molecular mobility has increased enough that the large distances separating the molecules might be surmounted. At least one of these transitions and possibly both should be detectable by careful esr measurements. Investigation into these possibilities is presently being conducted.

In conclusion, the solid state polymerization of N-(p-bromophenyl)dimethacrylamide yielded a soluble, linear polymer containing a large percentage of both five- and six-membered rings. The X-ray diffraction analysis of the crystalline monomer indicated that it crystallized in a conformation which would favor cyclization over intermolecular propagation. The low molecular weight of the polymer obtained could be explained by the large distances separating the reacting sites. Electron spin resonance measurements on irradiated polycrystalline samples indicated that a large amount of radical centers were generated by the irradiation and that they would persist for long times in the absence of external disturbance, which indicated that polymerization might continue indefinitely in the crystal lattice.

CHAPTER IV
SOLUTION INVESTIGATION

Results

Since so much information had been obtained about the monomer in the crystal study of N-(p-bromophenyl)dimethacrylamide, it was of interest to extend the investigation to its solution behavior. One more criterion for proving that the solid state reactions were controlled by the crystal lattice might be satisfied by a demonstration that these processes were different from those occurring in solution. Contribution of the monomer's crystalline conformation to that in solution could also yield some insight into its ground state solution properties. With this thought in mind the changes in the infrared spectra of the monomer were monitored for the change of phase from solid state to solution. Polymerization studies were also conducted using free radical and anionic initiation. It was thought that examination of the polymers resulting might provide information concerning the processes that led to their formation.

Spectral Analysis

Since the wavelengths at which carbonyl stretching vibrations occur are so affected by the environment of the chromophore, the infrared spectra of the monomer were compared when the monomer was in the solid phase (KBr pellet and Nujol mull) and in solution in benzene (dielectric constant, $\epsilon = 2.274$), chloroform ($\epsilon = 4.726$), and acetonitrile ($\epsilon = 38.8$). The absorption range, 1600 - 1800 cm^{-1}, over which carbonyl stretching vibrations generally occur is shown for each of the spectra in Figure 9.

Polymerization Studies

Free radical initiation - The free radical initiated polymerization of N-phenyldimethacrylamide has been reported elsewhere.[9, 40, 84] In this work the polymerization of N-(p-bromophenyl)dimethacrylamide is reported along with the effect of reaction conditions such as polarity of the medium and the temperature of the polymerization on the structure of the polymer formed.

In all polymerizations performed by free radical initiation a linear soluble polymer was obtained. Spectral investigation of said polymers indicated no residual unsaturation. The effect of temperature on the polymer structure was investigated by performing the AIBN-initiated reactions in benzene in sealed evacuated polymerization tubes. The temperatures were maintained at 58° and 114° for 24 hours. The high resolution pmr spectra of the polymers isolated are given in Figure 10. Comparison of the methyl shifts at δ 1.5 and δ 1.7 with those reported by Butler and Myers[40] for poly(N-phenyldimethacrylamide) indicated that a large percentage of five-membered ring was formed in the polymerization at lower temperature. Nearly doubling the reaction temperature, however, resulted in a stronger preference for the formation of six-membered ring than for five-membered ring. The estimated percentages of five- and six-membered

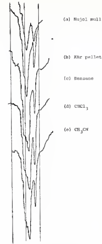


Figure 9· Infrared Spectra of N-(p-Bromophenyl)dimethacrylamide in (a) Nujol mull, (b) KBr pellet, (c) Benzene (0.24 M), (d) Chloroform (0.24 M); (e) Acetonitrile (0.24 M)

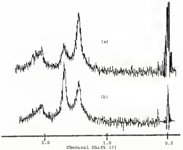


Figure 10: The PMR Spectra (100 MHz) of Poly[N-(p-bromophenyl)dimethacrylamide] Polymerized in Benzene at (a) 58°C and (b) 114°C. Spectrum was run at 150° (Nitrobenzene Solvent)

rings could be somewhat inaccurate, however, if the differences in methyl shifts for the various stereoisomers available to both ring sizes were large. Further investigation of the spectra with a higher resolution spectrometer might enable the separation of the various stereoisomers and therefore make the assignments more definitive.

The effect of the polarity of the medium on the polymer structure was studied by polymerizing N-(p-bromophenyl)-dimethacrylamide in dimethylformamide and comparing the polymer obtained with that formed in benzene at a comparable temperature. The AIBN-initiated polymerization yielded a linear soluble polymer whose high resolution pmr spectrum is given in Figure 11. Again, a preponderance of five-membered ring was formed at relatively low reaction temperature.

The polymerization conditions and results are summarized in Table 18. Analysis of the polymers by gel permeation chromatography yielded the chromatograms shown in Figure 12.

Ionic initiation - The anionic polymerization of N-(p-bromophenyl)dimethacrylamide was attempted using two initiating systems. The conditions used and the results of the polymerization attempts are summarized in Table 19. In all attempts the debromination of the aromatic ring was highly favored over the attack on the carbon-carbon double bonds. In the case of n-butyllithium the monomer presumably underwent a metal-halogen exchange as shown below. Once formed, the aryl anion XIV was then able to initiate

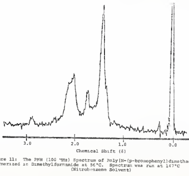


Figure 11: The PMR (100 MHz) Spectrum of Poly[N-(p-bromophenyl)dimethacrylamide Polymerized in Dimethylformamide at 56°C. Spectrum was run at 147°C (Nitrobenzene Solvent)

Table 18

Solution Polymerizations of N-(p-Bromophenyl)dimethacrylamide

Solvent[a]	ϵ[b]	T(°C)	Reaction Time (hr)	Conversion (%)	5-Membered[c] (%)	6-Membered[d] (%)
Benzene	2.274	58	24	34.0	80	20
Benzene	2.274	114	24	27.6	42	58
Dimethylformamide	36.71	56	22	23.2	81	19

[a] [M] = 0.5M; AIBN = 1%

[b] Dielectric constant at 25°

[c] Determined by planimetry of the methyl resonances (pmr) at δ 1.5

[d] Determined by planimetry of the methyl resonances (pmr) at δ 1.7

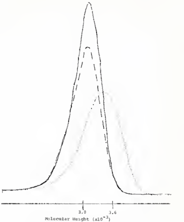


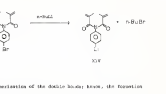
Figure 12: Gel Permeation Chromatograms of Poly(N-(p-Bromophenyl)dimethacrylamide Polymerized in Benzene at 58° (....), Benzene at 114° (—— ——), and Dimethylformamide (——)

Table 19

Attempted Anionic Polymerizations of N-(p-Bromophenyl)dimethacrylamide

Initiator	Solvent	Reaction Temperature	Reaction Time (min)	Results[a]
n-BuLi	THF	-78°C	10	Debromination of aromatic ring and formation of cross-linked polymer
$KOC(CH_3)_3$	THF	-78°C	10	No reaction
			30	No reaction
			60	No reaction
$KOC(CH_3)_3$	THF	Ambient	15	Debromination of aromatic ring - No polymer isolated

[a] [M] = 0.15 M; Initiator = 1 - 5%; Argon atmosphere



XIV

polymerization of the double bonds; hence, the formation of insoluble, cross-linked polymer. Potassium t-butoxide, however, was not nucleophilic enough to react with the double bonds. Warming the reaction to room temperature resulted in debromination of the aromatic ring and no detectable polymerization. Although potassium t-butoxide has been used to initiate polymerizations[85] of acrylamides and methacrylamides, in this case, it preferred to react with the aryl halide rather than with the double bond. Although not accomplished here, the anionic polymerization of N-(p-bromophenyl)dimethacrylamide should be possible. The initiating system should be much more nucleophilic than it is basic so that competition by the debromination reaction would not be a problem. Perhaps salts of mercaptans such as phenyl mercaptan might be suitable for the initiation reaction.

Discussion

Comparison of the infrared spectra of N-(p-bromophenyl)-dimethacrylamide in Nujol mull and KBr pellet indicated little difference between the two. It therefore seemed likely that the absorptions observed in the 1600 - 1800 cm^{-1} range for the monomer were actually indications of the environment of the carbonyls in the crystal. It has been observed previously that conformational changes could be induced by the pellet-grinding process[86] but this did not appear to be true in this study. It was concluded that the orientation of the imide carbonyls as determined by the X-ray diffraction study was characterized by the infrared spectra shown in Figure 9a and 9b.

Dissolution of the monomer in benzene, chloroform, and acetonitrile gave infrared spectra with the same fine structure as observed in the solid phase with the notable exception of the strong absorption which appeared at 1670 cm^{-1} in all three solution spectra. Several explanations for this new band could be proposed, the one of greatest interest being concerned with the conformation of the molecule. Once the restraints of the crystal lattice were lifted and rotations around single bonds could occur the monomer could orient so that the carbonyls would be in a different environment than they were in the crystal phase. The stretching vibrations of the carbonyls in this new environment might then occur at a new wavelength; hence, the new absorption band. The possibility that this band might be an overtone that for some reason did not appear in the solid phase should not, however, be completely overlooked.

The solution spectra of the monomer showed no obvious changes when the polarity of the medium was increased. This result would be consistent with the interactions within the monomer molecule being stronger than those between the monomer and the solvent. If the molecule first satisfied rather large electronic and steric requirements within itself subsequent interactions with the solvent might not be strong enough to appreciably change that orientation; at least not enough to be detectable by this infrared analysis. In 1968, Boyarchuk reported similar results in his study of the rotational isomerism of imide groups.[87] When the polarity of the solvent was increased di-isobutyramide and dimethacrylamide exhibited changes in their infrared spectra which he attributed to changes in conformation. He observed, however, very little noticeable change in the spectrum of N-methyldimethacrylamide for solvent changes from dioxane ($\varepsilon = 2$) to dimethylsulfoxide ($\varepsilon = 50$). He concluded that the planar conformations of the imide group of the dimethacrylamides were lower in stability due to the steric factors that would disrupt the coplanarity of the imide group and that an increase in the van der Waals radius of the nitrogen substituent would completely prevent the existence of even a distorted planar conformation as shown in Figure 13. The monomer, N-(p-bromophenyl)dimethacrylamide, might similarly minimize the repulsions within the molecule upon dissolution

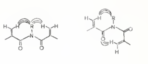


Figure 13: Steric Interactions in Dimethacrylamides

and these steric requirements might then make the largest demands on the orientation of the molecule. Consequently these conformations could be favored enough so that the change in the solvent's dielectric constant from 2 to 39 did not induce an orientation change large enough to be detectable by a spectrometer with that resolving power.

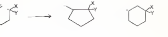
The free radical initiated polymerizations revealed several interesting features. Analysis of the polymers by pmr indicated that solvent polarity had little effect on the structure of the polymer although the yield was higher in benzene than in dimethylformamide. In both benzene and dimethylformamide there was a 4:1 preference for the formation of five-membered instead of six-membered ring at lower reaction temperatures. This was contrary to the initial reports on cyclopolymerization which proposed that the polymerization should proceed toward the formation of the thermodynamically more stable ring size which, in the case of 1,6-dienes, should be XV rather than XVI. The evidence that was offered for the formation of six-membered rings

XV

XVI

in these cyclopolymers[88] has however since been reinterpreted as also being consistent with the presence of five-membered cyclic units along the polymer backbone.[89] Thorough investigation of the structures of cyclopolymers has recently provided additional evidence that quite a few of these polymerizations proceed through the thermodynamically less stable intermediate, with the primary rather than the secondary or tertiary cyclized radical being formed.[90, 91]

In a review by Julia[92] the cyclization of 1-substituted 5-hexenyl radicals was reported to largely favor the formation of five-membered rings at lower temperatures as shown below. This preference was evident even though the cyclopentylmethyl isomer was less stable than the cyclohexyl isomer due to ring strain and eclipsing of the substituents. Julia proposed, as shown in Figure 14, that the cyclized



radicals may be of higher energy than the uncyclized substituted radical, which would make the reverse reaction a viable reaction pathway. The presence of six-membered ring

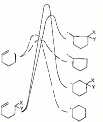


Figure 14: Suggested Reaction Paths for Cyclization with Stabilizing Substitutents X and Y

could then be explained by equilibration of the more rapidly formed cyclopentane radical (which was a result of kinetic control) to the more stable cyclohexane isomer (favored by thermodynamic considerations) before the hydrogen abstraction occurred.

Should kinetic control predominate in cyclopolymerization it would necessarily be dependent on the lifetime of the cyclized radical being too short for the equilibration to a thermodynamically more stable isomer to occur. This would be expected when the polymerization is characterized by a rapid propagation step or termination "freezes" a particular cyclic structure. Kinetic control might also affect the ring size distribution if the cyclization were an equilibrium process and if the primary radical were more reactive than the secondary or tertiary radical.

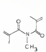
If the ring formed in the cyclization reaction is a heterocycle or contains a sp^2-hybridized atom, caution should be exercised in predicting whether the reaction product is a result of kinetic or thermodynamic control. In those instances the five-membered ring may actually be more favored from thermodynamic considerations. For example, a comparison of the oxidation rates of cyclopentanol and cyclohexanol indicates that the formation of cyclopentanone is much faster[93] than that of cyclohexanone. The introduction of the carbonyl group into the five-membered ring makes the geometry of that carbon planar, thereby relieving eclipsing strain with the substituents of the two adjacent carbons that had existed in the alcohol. Oxidation of cyclohexanol, however, distorts the molecule from the stable chair form it had occupied and introduces eclipsing strain between the substituents on the adjacent carbons. Likewise, a heteroatom such as nitrogen, oxygen, or sulfur may not necessarily orient with the same 109° tetrahedral angles that a methylene group would. This angular arrangement could be different enough that the five-membered ring could be more stable than the six-membered one. The resonance stabilization of the intermediate radical formed and the stability of the ring both contribute to the enthalpy of the cyclization process. Entropy of activation for the ring-forming reaction might likewise be a factor in determining the product distribution, particularly at higher temperatures.

The ring formed in the cyclopolymerization of N-(p-bromophenyl)dimethacrylamide contained both a heteroatom (nitrogen) and two sp^2-hybridized carbons. The large percentages of five-membered rings formed at low polymerization temperature could not therefore be assigned apriori to formation of the more or less stable isomer in the polymerization step even though the formation of a primary radical intermediate is generally considered to be less favored thermodynamically than that of the secondary or tertiary radicals. Nearly doubling the reaction temperature, however, of the polymerization in benzene increased considerably the percentage of six-membered ring, which led to the conclusion that it was the product favored thermodynamically.

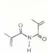
Therefore, it is likely that the low temperature products were a result of the faster cyclization process and that the six-membered ring could have arisen from equilibration of the more rapidly formed succinimide ring to the glutarimide repeating unit. Conceivably, if the above trend were to hold for the whole range of temperatures, the percentage of five-membered rings formed might be increased to as much as 100% by lowering the reaction temperature even further or by changing the initiating system to one that could be activated at room temperature.

It is rather difficult to explain why the propagating radical added more rapidly to the substituted end of the double bond than to the terminal end. Obviously the stability of the radical formed in the cyclization step was not the deciding factor. While the direction of cyclization has been justified by both electronic[30, 94] and steric[95, 96] interactions, it has also been suggested[97] that more conformations are available for the formation of a cyclopentylmethyl than for a cyclohexyl ring. In a review by Struble, Beckwith, and Gream[98] it was proposed that the interaction of the unpaired electron with the lowest unoccupied orbital of the unsaturated double bond determined the course of the free radical addition reaction. It was expected that bond formation would occur at that end of the double bond more readily approached vertically by the attacking radical.

Myers[99] postulated that the most probable conformation for N-methyldimethacrylamide was XVII and for dimethacrylamide was XVIII. If he assumed that after the propagating chain added to one methacryl group the other retained its s-cis



XVII

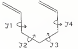


XVIII

or s-trans conformation until cyclization occurred, the structure of the polymers he obtained could be explained. No matter which methacryl group the propagating radical attacked in XVII the remaining one would be in a s-cis orientation. Rotation about the N-C bond would most likely result in the formation of five-membered ring. For XVIII he acknowledged that there were two possibilities: (1) addition initially to the s-trans methacryl group with the resultant formation of five-membered ring or (2) addition to the s-cis methacryl group and subsequent cyclization to six-membered ring. He attributed the cyclopolymerization of dimethacrylamide to give predominantly six-membered rings to the greater reactivity of the s-cis methacryl group.

Although the conformation of N-(p-bromophenyl)dimethacrylamide was fairly accurately known in the solid state the infrared analyses presented some evidence that could be explained by imide orientation changes when the compound was dissolved. It was therefore difficult to predict precisely the orientation of the monomer before it reacted with the initiating or propagating radical species. The steric interactions between one double bond and the methyl or the hydrogens on the terminal methylene of the other carbon-carbon double bonds should be quite large. The exact preorientation of the two double bonds for five- or six-membered ring formation without appreciable bond rotations was not likely. If, however, the molecule existed in a conformation that minimized these steric repulsions in the ground state, initiation of one of the double bonds and a subsequent bond rotation could lead to reaction with the more accessible carbon in the second double bond. If that closer carbon were the β-carbon, five-membered ring would be formed faster in the cyclopolymerization reaction.

In a 1,6-diene there are generally quite a few degrees of rotational freedom available to the molecule as a whole. Predictions based on a monomer retaining all but one rotational orientation during a reaction should therefore be more with caution. For example, the possible rotation axes of the carbon chain in 1,6-heptadiene are labelled in XIX. After initiation of one of the double bonds rotations around $\tau 1$, $\tau 2$, $\tau 3$, and $\tau 4$ could all conceivably occur before the



XIX

second double bond could be presented to the secondary radical in a conformation that would favor the cyclopolymerization reaction. With all these degrees of freedom either the α- or β-carbon of the double bond might approach the radical site readily and any attempts to predict the predominant route would be unwarranted. (This argument presupposes that there is no preorientation of the two double bonds for the cyclization reaction.)

In N-(p-bromophenyl)dimethacrylamide the chain probably is not quite so flexible. One factor that should certainly limit the rotational freedom of the molecule is the energy barrier for rotation around the nitrogen-carbonyl bond of the amide group. Generally these are considered to be quite high since the rotation would necessarily involve the disruption of pi cloud delocalization throughout the system. Constraints should also be made by the rather large steric requirements of the nitrogen substituent, the phenyl ring. The orientation of the two methacryl groups would probably be one in which their interaction with the phenyl ring would be minimized. Still a third restriction for rotation would be made by the two bulky methacryl groups themselves. A large energy barrier for those rotations which resulted in close approach of the two methyls or two methylene groups would be expected. It is not improbable that these steric requirements would limit severely the number of energetically-favorable conformations that would be available to the monomer. It is also not improbable that one of the methacryl groups might approximately maintain the same orientation until approached by the reacting species, which could favor the formation of one ring size over another in the cyclopolymerization reaction.

In conclusion, the distribution of the ring sizes in the polymer formed by solution polymerization was quite different from that formed by solid state polymerization. This provided additional evidence that the latter processes were governed to some extent by the restraints of the crystal lattice and that the molecular motion was not as free as it might be in solution. Almost certainly, however, the solution processes were also affected by the orientation of the molecule, that orientation being somewhat restricted by the large steric requirements within the molecule. In order to determine the relative importance of these steric requirements on the molecule it was decided that a quantum mechanical conformational analysis of the monomer might be of value. The results are given and discussed in the following chapter.

CHAPTER V
CONFORMATIONAL ANALYSIS

The Method

More and more frequently during the last decade organic chemists have resorted to the use of quantum mechanical methods in the investigation of conformations of large molecules. Many of these systems are, however, beyond the grasp of ab initio methods due to the large number of electrons involved. These large systems would require large numbers of basis functions for an even moderately accurate description of the molecular electronic environment, leading to the necessity of dealing with very large matrices and integrals within the Hartree-Fock approximation. Such calculations would very quickly become numerically difficult and economically not feasible. Consequently, semiempirical molecular orbital methods have generally been the methods of choices for calculations on larger molecules. These methods give qualitatively reasonable results and decrease appreciably the time required for calculating the energy of each conformation.

Methods such as Extended Huckel (EH)[100, 101] and complete/incomplete neglect of differential overlap (CNDO/INDO)[102, 103] treatments have been used previously for conformational analyses but EH generally exaggerates rotational energy barriers whereas CNDO/INDO predicts rotational energy barriers that are too low. More realistic results in conformational energy mapping have been obtained using a perturbative configuration interaction with localized orbitals (PCILO) method [104-107]

The program PCILO calculates the electronic ground state energy and the one particle density matrix. Essentially it looks at the molecule as an assembly of two center, two electron molecules (chemical bonds) in interaction, the interaction being treated by perturbation theory in an antisymmetrized basis. The method relies on four fundamental steps:

(1) building up the bonding and antibonding orbitals

(2) The antibonding orbitals are used for the construction of Slater determinants corresponding to excited configurations.

(3) The bonding orbitals are used to construct a Slater determinant which is the zeroth order wave function for the molecule.

(4) In the basis of all these determinants the molecular Hamiltonian is represented by a configuration interaction matrix. The eigenvalue and eigenvector are calculated by a Rayleigh-Schrödinger perturbation series.

The program in its present form applies the zero differential overlap (ZDO) simplification in order to force the starting set of bonding orbitals to be orthogonal. The application of CNDO II approximations for the molecular integrals further simplifies the calculations. A more detailed discussion of the theory may be found in a review by Pullman and Pullman[108] or in the original papers.[104-107]

The PCILO method has a strong chemical nature, with chemical assumptions being introduced at the beginning of each calculation. The method has been widely applied to large molecules with numerous degrees of freedom. The most striking applications have been done by B. Pullman and co-workers on biomolecules. Several recent reviews on amino acid residues and dipeptides,[108] pharmacologic compounds,[109] and solvation problems[110] indicate the applicability of the method. In some cases PCILO has uncovered stable conformations that have later been confirmed by experiments. At the very least it is an excellent exploratory tool—it allows a systematic search for the most likely conformers which may, in some cases, be confirmed by *ab initio* calculations.

Since the conformations of dimethacrylamides have been the subject of several investigations[40, 42, 87] as well as this study, it was of interest to calculate the relative energies of the conformations of N-(p-bromophenyl)dimethacrylamide. The atomic positions were obtained from the crystal coordinates determined earlier in this study. The standard IUPAC definition for dihedral angles[111] was used in determining the PCILO input.

Results and Discussion

Since the PCILO version used deals only with elements of the first row it was necessary to substitute for bromine in N-(p-bromophenyl)dimethacrylamide for the calculations. Self-consistent field (SCF) calculations on mono-substituted benzenes[112] indicated that the hydroxy group more nearly resembled bromine of any of the choices in its effect on the electron density localized on the atoms in the benzene ring. Therefore, subsequent calculations were performed with a hydroxy group para to the nitrogen and oriented so that a lone pair was parallel to the pi cloud of the benzene ring. Standard bond angles and lengths[113] for the hydroxy group were used as input for the program. The molecule used for the calculations is displayed in Figure 15 with the axes of rotation labelled $\tau1$, $\tau2$, $\tau3$, $\tau4$, and $\tau5$.

Discussion of the results should be prefaced with the reminder that the energies calculated do not necessarily reflect the absolute energies of the conformers but are merely valuable for relative comparisons of the effects of conformation changes in the energy of the conformer.

As is shown in Table 20, preliminary calculations demonstrated very rapidly that the energy of the crystal conformation (as well as the energy of many other conformations) could be appreciably lowered by a rotation of 35° around $\tau5$. This rotation served to orient the phenyl ring in a plane perpendicular to that containing the following atoms:

$$\begin{array}{c} C7'\text{-}N\text{-}C7 \\ | \\ C4 \end{array}$$

Subsequent calculations were made with that perpendicular arrangement of the phenyl ring. The energies calculated thereafter should not be affected by preferential interaction between the phenyl ring and one of the methacryl groups.

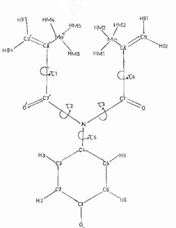


Figure 15: Model Used in the PCILO Calculations of N-(p-Bromophenyl)dimethacrylamide with and Axes of Rotation Defined

Table 20

Preliminary PCILO Calculations

Rotation Increment from Crystal Conformation	Energy (kcal)
0	-111274.00
$\tau 5 = 35°$	-111288.94

The initial investigation centered around a comparison of the relative energies of the possible coplanar orientations of the imide groups. The results obtained for the trans-trans, trans-cis, and cis-cis orientations as well as the effect of the methacryl conformation on the energies are given in Tables 21, 22, and 23, respectively. Since it was expected that large steric interactions existed between the methacryl groups, the effect of twisting one or both of the groups to a dihedral angle of 90° with respect to the C7'-N-C7 plane was investigated. These results are given in Tables 24, 25, 26, and 27. The search for conformations that were lower in energy than the crystal conformation and did not orient in a planar arrangement of the imide or methacryl groups revealed the orientations described in Table 28.

It was immediately obvious from an examination of the data presented that the monomer did not crystallize out in its lowest energy conformation. This is not too surprising, though, since the atomic and molecular interactions that govern the conformation of the molecule in solution do not

Table 21

Planar Trans-Trans Imide Conformer with Rotations of 90° Around τ1 and τ4

Conformer Number	Conformer[a]	Energy (Kcal)	Dipole Moment (debyes)
(1)		-111148.44	3.9346
(2)		-111271.50	4.3704
(3)		-111226.62	4.0019
(4)		-111195.69	4.2073
(5)		-111288.44	4.8901
(6)		-111273.75	4.3837
(7)		-111178.56	3.6854
(8)		-111271.19	4.1747
(9)		-111256.50	3.7510

[a] Where R =

Table 22

Planar Trans-Cis Imide Conformer with Rotations of 90° Around $\tau 1$ and $\tau 4$

Conformer Number	Conformer	Energy (Kcal)	Dipole Moment (debyes)
(10)		-106770.69	2.7901
(11)		-106862.69	3.0500
(12)		-106847.87	3.1163
(13)		-111199.37	1.4835
(14)		-111291.50	1.8152
(15)		-111276.94	1.8599
(16)		-108783.12	3.0547
(17)		-108875.06	3.3146
(18)		-108860.00	3.3825

[a]Where R = - -OH

Table 23

Planar Cis-Cis Imide Conformer with Rotations of 90° Around τ1 and τ4

Conformer Number	Conformer[a]	Energy (Kcal)	Dipole Moment (debyes)
(19)		-102098.00	1.2123
(20)		-107144.81	3.1184
(21)		-96818.12	5.2358
(22)		-107191.81 -107208.06[b]	2.3096 3.2407[b]
(23)		-109583.50 -111191.37[b]	5.4526 3.9713[b]
(24)		-108613.75 -108629.06[b]	5.4526 5.6492[b]
(25)		-97819.87	4.2298
(26)		-106553.62	4.8291
(27)		-833961.87	11.8729

[a] Where R = OH [b] Where τ1 is rotated 180°

Table 24

Planar Trans-Skew Imide Conformer with Rotations of 90° Around τ1 and τ4

Conformer Number	Conformer[a]	Energy (Kcal)	Dipole Moment (debyes)
(28)		-111183.19	3.1149
(29)		-111276.19 -111275.00[b]	3.0472 3.2687[b]
(30)		-111260.69	3.0953
(31)		-111189.75 -111189.81[b]	3.3498 2.7648[b]
(32)		-111266.12 -111289.87[b]	3.3497 2.8707[b]
(33)		-111266.12 -111267.37[b]	3.3497 2.7326[b]
(34)		-111188.56	2.8715
(35)		-111280.94 -111279.62[b]	2.8195 3.0114[b]
(36)		-111266.31	2.8100

[a] Where R = -OH, [b] Where τ4 is rotated 180°

Table 25

Planar Cis-Skew Imide Conformer with Rotations of 90° Around τ1 and τ4

Conformer Number	Conformer[a]	Energy (Kcal)	Dipole Moment (debyes)
(37)		-111205.37	3.5042
(38)		-111275.50 -111276.94[b]	3.2648 3.0131[b]
(39)		-111266.12	3.2326
(40)		-111132.25	3.5234
(41)		-111224.44 -111281.69[b]	3.3023 3.2343[b]
(42)		-111253.69	3.8126
(43)		-111213.62	3.6008
(44)		-111280.62 -111280.69[b]	3.4941 3.2796[b]
(45)		-111271.36	3.4276

[a] Where R = -OH, [b] Where τ1 is rotated 180°

Table 26

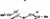
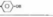
Cis Skew-Skew Imide Conformer with Rotations of 90° Around τ1 and τ4

Conformer Number	Conformer[a]	Energy (Kcal)	Dipole Moment (debyes)
(46)		-110934.62	3.5725
(47)		-111266.50 -111266.00[b]	3.7551 3.7081[b]
(48)		-111140.31	3.7827
(49)		-111263.31	3.7855
(50)		-111271.31 -111253.23[b]	3.9278 3.8441[b]
(51)		-111271.50	3.7920
(52)		-111104.00	3.5905
(53)		-111271.12 -111271.94[b]	3.5972 3.6122[b]
(54)		-111178.41	3.5472

[a] Where R = - -OH, [b] Where τ1 is rotated 180°

Table 27

Trans Skew-Skew Imide Conformer with Rotations of 90° Around τ1 and τ4

Conformer Number	Conformer[a]	Energy (Kcal)	Dipole Moment (debyes)
(55)		-111268,31	0,8555
(56)		-111270.25	1.0034
(57)		-111271.00	0.8741
(58)		-111273.06	1.3427
(59)		-111275.50	1.4666
(60)		-111276.12	1.3609
(61)		-111272.06	1.2315
(62)		-111275.37	1.4308
(63)		-111275.44	1,2664

[a]Where R = -OH

Table 28

Conformers Generated by Rotations from the Crystal Conformation

Conformer Number	Rotation Increment From Crystal 1	2	3	4	5	Energy (Kcal)
(64)	20				35	-111289.69
(65)	20	20			35	-111288.94
(66)			40		35	-111284.81
(67)			180		35	-111285.44
(68)		60	180		35	-111286.00
(69)		90	90	90	35	-111282.12
(70)		170			35	-111291.00
(71)		170		10	35	-111290.50
(72)		175			35	-111291.19
(73)		180			35	-111291.06
(74)	-10	180			35	-111291.69
(75)	-10	180		10	35	-111291.19
(76)		-160			35	-111288.56
(77)		180	180		35	-111288.19
(78)		151[a]	180		35	-111286.94
(79)		180	146[b]		35	-111224.81
(80)		151[c]	146[c]		35	-111183.44
(81)		151[d]			35	-111271.31
(82)			146[e]		35	-111282.81

[a] First amide group planar, cis-trans orientation of imide group

[b] Second amide group planar, cis-trans orientation of imide group

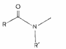
[c] Both amide groups coplanar, cis-trans orientation of imide group

[d] First amide group planar, cis-cis orientation of imide group

[e] Second amide group planar, cis-cis orientation of imide group

have the same relative importance in the solid phase if the molecules are to pack efficiently at all. Perhaps one of the most dramatic examples of this phenomenon is the difference between the conformations of biphenyl in the solid and liquid phase. In solution the two phenyl rings are oriented perpendicularly to each other. However, in the crystalline phase, in order to allow efficient packing of the molecules, the two phenyl rings orient in a coplanar arrangement.[114] Therefore, crystal packing forces may often supersede the van der Waals and electronic interactions in the molecule.

The calculations revealed certain recurring effects of conformational changes on the energy of that conformation. Perhaps the first to be noted was the interaction of the methacryl group with the nitrogen substituent. When the amide group was in a trans orientation as shown below, the lowest energy conformers were always those in which the carbon-carbon double bonds of the methacryl group were oriented



in a plane perpendicular to the carbonyl, thereby minimizing the interaction of the methyl and methylene with the phenyl ring. This was demonstrated by examination of the conformational changes (1)→(2), (1)→(4), (1)→(5), (7)→(8), (18)→(17), (15)→(14), (12)→(11), etc. There was obviously a great deal of steric interaction between the carbonyl substituent and the nitrogen substituent. This trend was further borne out in the clear preference of the methacryl group for the s-trans orientation which placed the terminal methylene near to the phenyl ring rather than in the s-cis orientation which would place the bulkier methyl group nearer to the phenyl. This effect was noted in the conformational changes (1)→(3), (1)→(7), (1)→(9), (16)→(18), (13)→(15), (10)→(12), and (10)→(18).

A cursory examination of the three coplanar imide arrangements revealed a general preference of the monomer for the trans-trans orientation. One major factor contributing to this preference over the trans-cis isomer was the rather large interaction in the latter conformer between one methacryl group and the carbonyl of the second methacryl group. When the carbon-carbon double bond was rotated 90° to orient in a plane perpendicular to the carbonyl and thereby decrease the steric repulsions with the second carbonyl [(18)→(16), (17)→(14), and (16)→(13)] the energy of the conformation lowered considerably. In fact, the lowest energy conformation found for all the coplanar imide arrangements was (14) in which there was a trans-cis arrangement of the imide group and both carbon-carbon double bonds were perpendicular to the carbonyls. This conformation minimized the repulsions between one methacryl group and the second carbonyl and between the other methacryl group and the phenyl ring. Only 3 kcal lower, however, was conformation (5) in which the imide group was in a trans-trans orientation and both carbon-carbon double bonds were perpendicular to their respective carbonyls. It is interesting that these two conformations were reasonably similar in energy when it might be predicted that the electronic repulsions between the carbonyls would make the trans-trans orientations much less favored. In a Molecular Mechanics (MMI) calculation on the monomer performed independently by Dr. John Turner of the Textile Fibers Department of DuPont Pioneering Research Laboratories and described in Appendix II, the lowest energy conformers were found to be those with a trans-trans orientation of the imide group. They were admittedly uncertain, however, that their minimization process had yielded the lowest energy conformer.

Predictably, the energies of the cis-cis coplanar arrangement reflected the large steric interactions of the two bulky methacryl groups. Although making the two carbon-carbon double bonds perpendicular to the carbonyls lowered the energy of the conformations considerably [(19)→(20), (19)→(22), and (19)→(23)] these were still fairly high in energy compared to those with a trans-trans and trans-cis imide group. It is not likely, therefore, that the monomer would orient in this manner once the crystal packing restraints were lifted. A 180° rotation around τ1 relieved the large steric interaction between the two methyl groups in conformer (23) considerably. That one rotation lowered the energy of that conformation by 1607.87 kcal, a notable decrease even though it was still quite high in energy. Obviously the steric requirements of that conformer were so high that the stabilization from the parallel overlapping arrangement of the two pi clouds and partial bonding that might be envisioned to result from that overlap is not enough to overcome the steric demands of the conformer. The overlap of the pi clouds is demonstrated in Figure 16.

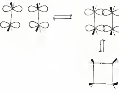


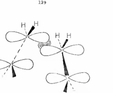
Figure 16: Overlap of the Pi Clouds in Conformer (23)

The effect of orienting one of the methacryl groups perpendicular to the imide plane is detailed in Tables 24 and 25. This rotation should tend to stablize those trans-trans isomers that had a considerable interaction between the nitrogen substituent and the methacryl group by rotating the methacryl group away [(1)→(28), (2)→(29), and (3)→(30)]. Similarly, the trans-cis isomers that were chiefly affected were those that had a large interaction between the methacryl group and the second carbonyl which could be relieved by the 90° rotation of the methacryl group [(18)→(36), (17)→(35), (11)→(29), and (12)→(30)]. Notably, the conformational changes (15)→(33), (14)→(32), and (13)→(31) were to higher energy conformations. Since in the trans-cis isomers, [(15) (14), and (13)], the carbon-carbon double bond had been rotated to minimize the repulsion with the carbonyl group, a subsequent skewing of the methacryl group only served to raise the energy of the respective conformers. Probably no great steric relief was obtained and electronic stabilization was diminished by the decrease in the delocalization of the pi cloud of the imide group. A similar effect was observed for the conformational changes (4)→(31), (5)→(32), and (6)→(33).

The energies of the cis-cis conformers were lowered considerably in every instance by rotating the methacryl group 90°, an effect which supported the hypothesis that these conformers were primarily destabilized by the large steric interactions between the bulky methacryl groups.

The two conformers (38) and (44) were relatively low in energy, the steric interactions between the methacryl groups had been minimized and the two carbon-carbon double bonds were fairly separated in space. Initiation of one of the double bonds and a rotation around the imide nitrogen-carbonyl bond could, however, very easily lead to the formation of the cyclic repeating unit observed in the polymerization reaction.

It is worthy of note that the energy of conformer (41) was lowered by 57.25 kcals by a rotation of 180° around τ1. There was no other similar effect from this rotation on the energies of any conformer in the series (37)-(45). The small energy changes for conformers (39) and (44) indicated that there was apparently no large interaction with the bulk of the molecule being relieved and molecular models indicated that there was little steric relief between the two methacryl groups gained by this rotation. One quite reasonable explanation for this large energy change hinges on the change in the relative position of the two pi clouds. In the first orientation of conformer (23) the two double bonds were fairly separated in space and the large distance between them made overlap of the pi clouds unlikely. With the 180° rotation around τ1, however, the two double bonds were placed in close proximity of each other, similar to that shown below. In this particular orientation, the two terminal p-orbitals of the double bonds were nearly in a colinear arrangement and the substituents of the double bonds were oriented so that steric interactions were minimal (a situation

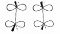


quite contrary to that found in conformer (23) which might also be expected to show similar stabilization from the pi cloud overlap). Unfortunately the program does not provide the overlap integrals in the output so that the extent of this overlap could be estimated.

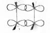
If the energy change of conformer (23) was indeed a reflection of an electronic stabilization it might be interpreted as evidence for the through-space non-conjugated interaction which has been proposed[30] to exist between the double bonds of 1,6-dienes. This interaction, if it existed, would be expected to preorient the double bonds in a direction which would favor the cyclization reaction after initiation by a free radical. In N-(p-bromophenyl)dimethacrylamide, however, the large steric and electronic interactions within the molecule make fairly severe demands on the orientation of the molecule. In spite of this large energy lowering in conformer (41) and apparent stabilization of the isomer there were other conformers found that were as much as

10 kcal lower in energy. Apparently, there is some evidence, therefore, for interaction through space between these two double bonds, but other conformations might be more favored for their relief of other strain within the molecule. Further investigation into this phenomenon will be carried out in the future on a somewhat simpler system, 1,5-hepta-diene, on which the early proposals for electronic interaction were based.[30] The severe steric interactions present in N-(p-bromophenyl)dimethacrylamide would not be expected to exert such a large influence on the conformer's energy in this case and results might be found that would shed some light on this still puzzling question in cyclopolymerization reactions.

When both methacryl groups in N-(p-bromophenyl)dimethacrylamide were skewed 90° from the imide plane and were in a cis orientation with respect to each other, only those conformers which allowed a perpendicular arrangement of the carbon-carbon double bonds to the carbonyls (47), (49), (50), (51), and (53) were again relatively low in energy. When τ1 was rotated 180° in conformers (47), (53) and (50), the energy of the conformation of (50) raised 18.06 kcals when the two double bonds were no longer parallel to each other and no longer oriented in a direction that would favor the through-space overlap of the pi clouds. Since (47) and (53) showed little change in energy with this rotation the energy change probably did not reflect a change in the steric interactions with the remainder of the molecule. Molecular models indicated that the two double bonds were oriented so that the substituents were fairly separated in space. Once again it is not unreasonable to assume that this energy change was due to an interaction between the two pi clouds. It should be remembered that the electron density in a bond is in the form of a distribution and not merely localized charge density. When two pi clouds are oriented as they are in conformer (50) and as drawn in XX below, if the two are close enough in space it is almost academic whether they are represented by XX or XXI. It is therefore again not



XX



XXI

unreasonable that the calculations should predict that the orientation in which the pi clouds could overlap would be lower in energy than when this overlap was not possible.

When the two methacryl groups were skewed trans to one another as shown in Table 27, the energies of the conformers varied only over a range of 8 kcal. Twisting the two bulky groups away from each other obviously satisfied the major steric requirements of that isomer and the two groups were far enough away from each other that no major interactions were relieved by rotations around $\tau1$ and/or $\tau4$. These minimizations of steric repulsions were probably accomplished at the expense of electronic stabilization by delocalization of the imide pi cloud. Somewhat lower energies were observed for those conformations in which one of the amide groups was coplanar with the imide plane.

The conformers discussed above were all generated by changing the orientation of the atoms in the crystal conformation to the new orientations and then performing the rotations around $\tau1$ and $\tau4$. This is by no means a complete description of the isomers available to the monomer and possibly may not even predict accurately the trend toward the conformer of lowest energy. In its present form, PCILO is designed so that all rotation axes, as well as the rotation increment, are defined at the beginning of the calculations. The energies and dipole moments of the conformations resulting from all possible combinations of these rotations are then calculated. Since there were at least five axes of interest in N-(p-bromophenyl)dimethacrylamide and a rotation increment should probably be no greater than 20°, a total of $9^5 = 59{,}049$ calculations would have been performed if the study had been executed in this manner.

The computing time required and the cost of such an approach to this conformational analysis would have been prohibitive and still, even with 20° increments, might not be definitive. Conformations other than those described in Tables 21-27 were investigated, however, by rotating around axes $\tau 1$ - $\tau 5$ from the original crystal coordinates. A partial list of some of the lower energy conformers is given in Table 28.

Inspection of Table 28 once again emphasized that it is quite likely that the monomer would orient in a new conformation once the restraints of the crystal lattice were lifted. It is also obvious that many of the coplanar orientations could lower considerably in energy when they were allowed to skew slightly out of coplanarity and thereby minimize the steric repulsions. For instance, all of the cis-cis coplanar isomers in Table 23 were quite high in energy. However, a slight skewing out of that arrangement by the molecule resulted in very energetically favored orientations as shown by conformers (70), (75), and (77). In addition to being low in energy, those conformers (70)-(75) all were characterized by a very close alignment of the two carbon-carbon double bonds involved in the polymerization reaction. Since the two β-carbons were considerably closer to each other than any other two atoms, it could be very reasonably postulated that initiation of one of the double bonds and a fast cyclization reaction would almost certainly lead to cyclopolymer containing five-membered ring. It appears, therefore, that even such a sterically crowded molecule as N-(p-bromophenyl)dimethacrylamide could orient in a fairly low energy conformation that would favor formation of five-membered over six-membered ring. Once again, though, it should be restated that it is not certain by any means that this orientation would be the absolute lowest energy conformation available to the molecule. It was, however, one of several conformers found to be considerably lower in energy than many others investigated.

In summary, then, the calculations demonstrated the following:

(1) The monomer did not crystallize out in its lowest energy conformer.

(2) If the monomer were to exist with a coplanar arrangement of the imide group, it must be one such as (5) or (14) in which the two carbon-carbon double bonds were not arranged in a coplanar orientation so that they might minimize steric interactions with other parts of the molecule.

(3) The methyl group presented more of a steric interaction with the phenyl ring than did the hydrogens on the terminal methylene carbon. This factor tended to force the methacryl group, when planar, to exist in an s-trans orientation of the carbon-carbon double bond and the carbonyl when such steric interactions existed.

(4) The trans-cis orientation was slightly favored over the trans-trans when proper rotations of the carbon-carbon double bonds alleviated steric interactions with the remainder of the molecule (See conformers (4), (5), and (6) vs. conformers (13), (14), and (15)).

(5) The cis-cis coplanar arrangement was highly unlikely. Slight rotations out of the coplanar arrangement, however, created conformers that were as low in energy and, in some cases, lower than those cited above.

(6) Some energy lowering of conformers was exhibited that could be explained by an interaction through space of the two carbon-carbon double bonds.

(7) A conformation in which preorientation of the double bonds for formation of five-membered rings existed was found to be fairly low in energy. It is not certain, however, that this was the absolute lowest energy conformation available to the molecule. Still lower energy orientations might be accessible for the molecule that were not uncovered in this search.

Finally, it must be mentioned that calculations of this nature are, strictly speaking, valid for the gas phase of the molecule. Extrapolations of these results to solution processes must presuppose the absence of appreciable monomer-solvent or monomer-monomer interactions.

CHAPTER VI
SUMMARY AND DISCUSSION

The heart of this research dealt with the cyclopolymerization phenomenon, why and how it occurs. In specific, the relationship between the conformation of N-(p-bromophenyl)dimethacrylamide and its polymerization behavior in both the solid and solution phases was of interest. Could it be shown that the solid state polymerization of the monomer was a result of the monomer's orientation in the crystal lattice? How similar were these solid state processes to the solution behavior of the monomer? Could the solution polymerization of the monomer also be affected by its conformation? In attempting to answer these questions the investigation summarized below was undertaken.

Irradiation of the crystalline monomer with γ-rays from a cobalt-60 source resulted in the formation of a polymer that was 100% cyclized. Spectroscopic investigation of the polymer structure yielded evidence that both five- and six-membered rings were formed in the reaction. The X-ray diffraction study on the monomer revealed the following information about its conformation.

(1) The imide group roughly oriented with a cis-trans arrangement of the two carbonyls with respect to the nitrogen substituent. Neither of the carbonyl oxygens was coplanar with the imide plane, a factor which decreased the extent of delocalization of the pi cloud throughout the imide group.

(2) Neither of the two methacryl groups oriented with a coplanar arrangement of the carbonyl and the carbon-carbon double bond, which once again disrupted the pi cloud delocalization.

(3) Both methacryl groups oriented in a s-trans conformation as shown below.

(4) The two carbon-carbon double bonds oriented with a dihedral angle of 87.45° with respect to each other, a nearly perpendicular arrangement which almost completely ruled out the possibility of a through space nonconjugated interaction[30] between the two pi clouds in the solid state.

Calculations of the distances separating the reacting species in the lattice revealed that the intramolecular propagation route was always shorter than the intermolecular one by at least 0.4-0.7 Å. This large distance should almost certainly make the cyclization reaction favored over the intermolecular propagation so long as these relative orientations were maintained.

For several reasons it was impossible to predict the distribution of ring sizes in the cyclopolymer from the crystallographically-determined atomic positions. First of all, the two available intramolecular paths did not always differ widely in the distances separating potential reactors. Secondly, generation of the initiating or propagating species would almost certainly change these relative orientations at least slightly. Finally, the movement of the atoms from a distance of 4 Å to the 1.4 Å characteristic of the carbon-carbon single bond would make predictions based on that initial orientation somewhat untenable.

The esr measurement on the irradiated sample indicated that radical centers were generated by the ionizing radiation. Changes in the spectra with time were interpreted as being indicative of reactions occurring in the crystal lattice; continuing propagation or radical recombinations and terminations. The persistence of the esr signal over a long period of time was almost certainly indicative of the restricted mobility of the reacting species in the crystal lattice. With the assumption that the processes occurring in the solid state were radical in nature, it was proposed that even more valuable information about the initiating and propagating processes could be obtained from single crystal esr studies.

All available information, therefore, led to the conclusion that the solid state polymerization behavior of N-(p-bromophenyl)dimethacrylamide was controlled by the conformation of the monomer molecule in the crystal lattice. So long as disordering of the lattice did not occur and the relative distances separating the intramolecular and intermolecular reacting species were not altered drastically by the polymerization, the tendency of the monomer molecule to cyclize completely could be predicted from the orientation of the reacting double bonds.

The solution polymerization of the monomer by radical initiation also resulted in the formation of a polymer that was 100% cyclized. At low temperatures the formation of five-membered rings was favored over that of six-membered rings by a ratio of 4:1. As the temperature of the polymerization was increased, however, the formation of six-membered ring became more prevalent. At 114° the ratio of six-membered to five-membered ring had changed from the aforementioned 1:4 to 3:2. It was concluded that the five-membered ring fromed at the lower reaction temperature was a result of kinetic control of the reaction. Raising the temperature of the reaction changed the product distribution with a resultant increase in the thermodynamically-favored product, the six-membered ring.

Infrared analysis of the imide carbonyl stretching vibrations for the phase change from solid to solution revealed the appearance of a new absorption band with the dissolution of the monomer. Since the position of imide carbonyl absorption bands are generally known to be sensitive to changes in the chemical environment of the molecule, it was postulated that this new band could be indicative of a conformational change in the monomer molecule when the restraints of the crystal lattice were lifted. The solution spectra of the monomer were not noticeably affected by changes in the dielectric constant of the solvent from 2 to 39. This insensitivity to the polarity of the medium could be a reflection of rather severe steric restrictions within the molecule. If these interactions were stronger than those between the monomer and solvent the change in dielectric constant of the solvent might not induce enough of a change in conformation in the molecule to be detectable by the spectrometer used.

Subsequent investigation into the conformational restrictions in N-(p-bromophenyl)dimethacrylamide was made using a quantum mechanical perturbative configuration interaction with localized orbitals methods. Application of these results to the solution conformation of the monomer necessarily involved the assumption that the interactions between the monomer and other monomer or solvent molecules were negligible.

The calculations indicated that the conformation of the monomer in the crystal lattice was not one that minimized all the steric interactions within the molecule. It is likely, therefore, that the monomer would orient in a new conformation(s) upon dissolution. Contrary to predictions[42] the methacryl group, when planar, tended to occupy an s-trans orientation of the carbon-carbon double bond and the carbonyl to minimize steric interactions with the nitrogen substituent.

In no instance was a conformation with a planar arrangement of both the imide and methacryl groups a low energy conformation. In most cases a relatively low energy orientation could be attained by (1) keeping the imide group planar and orienting one or preferably both methacryl groups perpendicular to that plane or by (2) keeping the methacryl groups planar and twisting the imide group so that it was no longer planar.

Of the three major orientations containing a planar imide group, the lowest energy conformer was characterized by cis-trans orientation of the two carbonyls to the nitrogen substituent and the two carbon-carbon double bonds perpendicular to the imide plane. In the second lowest energy conformer both carbonyl oxygens were trans to the nitrogen substituent and the two carbon-carbon double bonds were again perpendicular to the imide plane. The least likely orientation in which the imide group was planar was that in which both carbonyl oxygens were cis to the nitrogen substituent. The large steric interactions between the two bulky methacryl groups destabilized all possible conformations with this orientation.

Low energy conformations were found in which neither the imide nor the methacryl groups were in a coplanar arrangement. Of particular note were several conformers with the two carbonyl oxygens roughly cis-cis to the nitrogen substituent. Since the energy of the conformer was so low the orientation was apparently quite stable. The two carbon-carbon double bonds were fairly close to each other with the shortest distance between the two β-carbons. Initiation of one double bond and a subsequent fast cyclization reaction could very plausibly result in the formation of a five-membered ring. While it is conceivable that other lower energy conformers of the molecule might exist that were not uncovered by this conformational analysis, the evidence obtained seemed to indicate that conformations of low energy were accessible to the monomer in which the prorientation of the double bonds would lead to the formation of five-membered ring faster than that of six-membered ring.

Though there exists much evidence today that radical cyclizations often proceed under kinetic control to the formation of five-membered rings, the explanations for why that should be the faster route are not nearly so clear. Why the less stable isomer should quite often be formed faster than the more stable six-membered ring is one of the still unsolved puzzles in cyclopolymerization reactions. In the case of N-(p-bromophenyl)dimethacrylamide it might be that the rather large steric restrictions in the molecule limit the number of conformations available to the monomer. Similarly those rotations which would involve close approach to the two methacryl groups would in many cases be characterized by a high energy barrier. Therefore preorientation of the monomer in a conformation in which the two β-carbons are fairly close to each other and steric interactions are minimized or an easy access to that orientation by single bond rotations might contribute considerably to the large percentage of five-membered rings in the solution polymer. With an increase in the reaction temperature, however, many of these previously forbidden rotations would become more probable. Preorientation of the double bonds for the formation of five-membered rings would then be less important at higher reaction temperatures than it had been at the lower ones. Product distribution would be expected to reflect this change.

It is interesting that, whereas other conformers of comparable energy achieved some stabilization from extended pi cloud delocalization in the planar imide group, the aforementioned "preoriented" conformer had no such stabilization. Neither the imide group nor the methacryl groups were planar. Why, then, should this conformer I be so stable when other isomers which likewise minimized steric repulsions in the molecule were not nearly so low in energy? Perhaps some stabilization could arise from the interaction of these two pi clouds through space. While the four carbon atoms in the double bonds are not colinear in this orientation the two double bonds are certainly close enough that at least partial overlap of their pi clouds is not unreasonable. Similar effects were observed for conformations in which the two double bonds were not nearly so close to each other. Yet the orientations favoring that overlap were much lower in energy than those in which no overlap could occur. Investigation of this effect in systems with less steric repulsions might provide some interesting corroboration of the proposed[30] through space interaction of the nonconjugated double bonds in dienes that cyclopolymerize.

In conclusion, the tendency of N-(p-bromophenyl)dimethacrylamide to cyclopolymerize in the solid state could certainly be explained by the monomer's conformation in the crystal lattice. Since there are such large steric repulsions within the monomer, its tendency to form a less stable product faster might also be due to conformational restraints in the solution phase. In answering some of the original questions this study also served to pose still more, namely those concerning (1) the actual observation of the solid state polymerization processes by single crystal esr and (2) further investigation of those preliminary indications of through space interaction between nonconjugated dienes by PCILO calculations on simpler dienes. Further work along these lines is in progress.

APPENDIX I

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR N-(p-BROMOPHENYL)DIMETHALRYLAMIDE

```
  L   FO    FC
H=   2, K=   0
  0 1373  -608
H=   4, K=   0
  0  430 -1422
H=   6, K=   0
  0 1261  1024
H=   8, K=   0
  0 1091  -194
H=  10, K=   0
  0 1812   423
H=  12, K=   0
  0 2198  -513
H=  14, K=   0
  0  492   420
H=  16, K=   0
  0  353   350
H=  18, K=   0
  0  828    45
H=  20, K=   0
  0 1348   203
H=  22, K=   0
  0 1835   834
H=  24, K=   0
  0 1033   354
H=  26, K=   0
  0  911  -344
H=  28, K=   0
  0  865  -285
H=  30, K=   0
  0  752  -253
H=  32, K=   0
  0  481    51
H=   0, K=   0
  2  876  1531
H=   1, K=   0
  2 1164  -824
H=   2, K=   0
```

```
  L   FO    FC
  2 1952  -710
H=   3, K=   0
  2 1758  -865
H=   4, K=   0
  2 2034 -1044
H=   5, K=   0
  2  780   876
H=   6, K=   0
  2  777   440
H=   7, K=   0
  2 1057  -113
H=   8, K=   0
  2 2018   958
H=   9, K=   0
  2  794  -137
H=  10, K=   0
  2  444  -887
H=  11, K=   0
  2  -51   -32
H=  12, K=   0
  2  182  -588
H=  13, K=   0
  2  485  -112
H=  14, K=   0
  2 1131   588
H=  15, K=   0
  2  288  -822
H=  16, K=   0
  2  115   220
H=  17, K=   0
  2  772   -87
H=  18, K=   0
  2  883   -49
H=  19, K=   0
  2  838    82
H=  20, K=   0
  2 1018  -219
H=  21, K=   0
```

```
  L   FO    FC
  2  179  -287
H=  22, K=   0
  2  874  -130
H=  23, K=   0
  2  184    85
H=  24, K=   0
  2  411    27
H=  25, K=   0
  2  932  -461
H=  26, K=   0
  2  177  -127
H=  27, K=   0
  2  858   -69
H=  28, K=   0
  2  214   -53
H=  29, K=   0
  2  -87   198
H= ,30, K=   0
  2  468    84
H=  31, K=   0
  2  349  -178
H=  32, K=   0
  3  437    88
H=   0, K=   0
  4  373   120
H=   1, K=   0
  4  333  -819
H=   2, K=   0
  4  988   828
H=   3, K=   0
  4  570  -658
H=   4, K=   0
  4  888  -942
H=   5, K=   0
  4 1801   441
H=   6, K=   0
  4  415  -233
```

```
  L   FO    FC
H=   7, K=   0
  4  902  -482
H=   8, K=   0
  4  733   871
H=   9, K=   0
  4  117  -602
H=  10, K=   0
  4 1015  -782
H=  11, K=   0
  4  175   251
H=  12, K=   0
  4  401  -372
H=  13, K=   0
  4  301   453
H=  14, K=   0
  4  287   211
H=  15, K=   0
  4  989   138
H=  16, K=   0
  4  470   255
H=  17, K=   0
  4  986    33
H=  18, K=   0
  4  180   -34
H=  19, K=   0
  4  588   189
H=  20, K=   0
  4  -81   -88
H=  21, K=   0
  4  180   -78
H=  22, K=   0
  4  237   184
H=  23, K=   0
  4  379    24
H=  24, K=   0
  4  -83    44
H=  25, K=   0
  4  330  -278
  L   FO   FC
H= 16, K=   0
  4  -88   95
H= 17, K=   0
  4  132  -37
H= 18, K=   0
  4  274 -119
H= 19, K=   0
  4  503  113
H= 20, K=   0
  4  188  -52
H=  0, K=   0
  6   85 -442
H=  1, K=   0
  6  327  -46
H=  2, K=   0
  6  507    1
H=  3, K=   0
  6  940 -256
H=  4, K=   0
  6  136 -358
H=  5, K=   0
  6  581  321
H=  6, K=   0
  6  -86  -41
H=  7, K=   0
  6  552  187
H=  8, K=   0
  6  -87  255
H=  9, K=   0
  6  752 -414
H= 10, K=   0
  6  666 -379
H= 11, K=   0
  6  381  178
H= 12, K=   0
  6  787 -280
H= 13, K=   0

  L   FO   FC
  6  848  251
H= 14, K=   0
  6  598 -183
H= 15, K=   0
  6  714   21
H= 16, K=   0
  6  188  257
H= 17, K=   0
  6  387 -183
H= 18, K=   0
  6  -82 -187
H= 19, K=   0
  6  231  -19
H= 20, K=   0
  6  -88 -185
H= 21, K=   0
  6  -88  185
H= 22, K=   0
  6  385   20
H= 23, K=   0
  6  403  -81
H= 24, K=   0
  6  180 -188
H= 25, K=   0
  6  437  -28
H= 26, K=   0
  6  145  163
H= 27, K=   0
  6  350   37
H=  0, K=   0
  8  841  -88
H=  1, K=   0
  8  -76  -33
H=  2, K=   0
  8  387  134
H=  3, K=   0
  8  130  -42
H=  4, K=   0

  L   FO   FC
  8  257  -30
H=  5, K=   0
  8  21K   26
H=  6, K=   0
  8  -78 -193
H=  7, K=   0
  8  -78  -81
H=  8, K=   0
  8  473  289
H=  9, K=   0
  8  203 -150
H= 10, K=   0
  8  829  368
H= 11, K=   0
  8  143   13
H= 12, K=   0
  8  572   88
H= 13, K=   0
  8  165  333
H= 14, K=   0
  8  427  125
H= 15, K=   0
  8  215  405
H= 16, K=   0
  8  -85 -181
H= 17, K=   0
  8  -87  -38
H= 18, K=   0
  8  380 -185
H= 19, K=   0
  8  -85   22
H= 20, K=   0
  8  321   42
H= 21, K=   0
  8  347  202
H= 22, K=   0
  8  388  -59

  L   FO   FC
H= 23, K=   0
  8  -81 -102
H=  0, K=   0
 10  530  217
H=  1, K=   0
 10  -85  -53
H=  2, K=   0
 10  147  -58
H=  3, K=   0
 10  -84  -44
H=  4, K=   0
 10  120   44
H=  5, K=   0
 10  -84 -117
H=  6, K=   0
 10  -82  120
H=  7, K=   0
 10  281  116
H=  8, K=   0
 10  203  -88
H=  9, K=   0
 10  279  165
H= 10, K=   0
 10  148  138
H= 11, K=   0
 10  -85 -181
H= 12, K=   0
 10  262    8
H= 13, K=   0
 10    -  -65
H= 14, K=   0
 10  117  -28
H= 15, K=   0
 10  150  -59
H= 16, K=   0
 10  -80  -32
H= 17, K=   0
 10  288 -188
```

```
  L    FO    FC       L    FO    FC       L    FO    FC       L    FO    FC
H=  2, K=   1       1  501   428        1  164    66      H=  9, K=   1
  0 1038  1037     H=  4, K=   1       H= 23, K=   1        2 1270   828
H=  4, K=   1       1 1369   551        1  283   -21      H= 10, K=   1
  0  841   108     H=  5, K=   1       H= 24, K=   1        2  283   118
H=  6, K=   1       1  278  -357        1  271   292      H= 11, K=   1
  0  194   772     H=  6, K=   1       H= 25, K=   1        2  105  -302
H=  8, K=   1       1 1195   697        1  140   -13      H= 12, K=   1
  0  892   -81     H=  7, K=   1       H= 26, K=   1        2  789  -488
H= 10, K=   1       1  458  -145        1  319   365      H= 13, K=   1
  0  156   365     H=  8, K=   1       H= 27, K=   1        2  668   186
H= 12, K=   1       1 1555  -288        1  276   248      H= 14, K=   1
  0  214   -91     H=  9, K=   1       H= 28, K=   1        2  697  -282
H= 14, K=   1       1  257   277        1  498    21      H= 15, K=   1
  0  374  -187     H= 10, K=   1       H= 29, K=   1        2  482   284
H= 16, K=   1       1  -52   239        1  127   -70      H= 16, K=   1
  0 1062   412     H= 11, K=   1       H= 30, K=   1        2  290   111
H= 18, K=   1       1 1061  -408        1  173    82      H= 17, K=   1
  0  846    80     H= 12, K=   1       H= 31, K=   1        2  299  -191
H= 20, K=   1       1  684    62        1  118    37      H= 18, K=   1
  0  -74  -158     H= 13, K=   1       H= 32, K=   1        2  321   -28
H= 22, K=   1       1  858  -213        1  -76   -17      H= 19, K=   1
  0  224   221     H= 14, K=   1       H=  1, K=   1        2  188   141
H= 24, K=   1       1 1452   208        2  202   413      H= 20, K=   1
  0  279   842     H= 15, K    1       H=  2, K=   1        2  238  -133
H= 26, K=   1       1  283   -38        2  804   840      H= 21, K=   1
  0  245    76     H= 16, K=   1       H=  3, K=   1        2  249     0
H= 28, K=   1       1 1414   216        2  870  1245      H= 22, K=   1
  0  189    78     H= 17, K=   1       H=  4, K=   1        2  129    80
H= 30, K=   1       1  208   207        2  351  -305      H= 23, K=   1
  0  -82    57     H= 18, K=   1       H=  5, K=   1        2  -83   138
H= 32, K=   1       1  571  -310        2 1267  -984      H= 24, K=   1
  0  -75   -63     H= 19, K=   1       H=  6, K=   1        2  325   130
H=  1, K=   1       1  -71  -238        2  653    34      H= 25, K=   1
  1  245  -584     H= 20, K=   1       H=  7, K=   1        2  -88    82
H=  2, K=   1       1  402   138        2  528   350      H= 26, K=   1
  1   53  1284     H= 21, K=   1       H=  8, K=   1        2  -66  -100
H=  3, K=   1       1  269   -84        2  887   283      H= 27, K=   1
                   H= 22, K=   1                            2  325  -319
  L    FO    FC
H= 28, K=    1
  2   -86   -69
H= 29, K=    1
  2   -88    78
H= 30, K=    1
  2   -64     5
H= 31, K=    1
  2   -82     4
H=  1, K=    1
  3  1272   112
H=  2, K=    1
  3  1171   711
H=  3, K=    1
  3  1287  -382
H=  4, K=    1
  3   392  1157
H=  5, K=    1
  3   -47   117
H=  6, K=    1
  3  1385   582
H=  7, K=    1
  3   762   111
H=  8, K=    1
  3   431   -84
H=  9, K=    1
  3  1680   536
H= 10, K=    1
  3   -55   -12
H= 11, K=    1
  3  1857   537
H= 12, K=    1
  3   563  -155
H= 13, K=    1
  3   886    83
H= 14, K=    1
  3   583    84
H= 15, K=    1

  L    FO    FC
  3   456    99
H= 16, K=    1
  3   401   148
H= 17, K=    1
  3   332   -16
H= 18, K=    1
  3   588  -261
H= 19, K=    1
  3   736  -122
H= 20, K=    1
  3   215   255
H= 21, K=    1
  3   788   -45
H= 22, K=    1
  3   -63   -98
H= 23, K=    1
  3   502    15
H= 24, K=    1
  3   374    32
H= 25, K=    1
  3   274    12
H= 26, K=    1
  3   338     7
H= 27, K=    1
  3   133   -14
H= 28, K=    1
  3   -83  -281
H= 29, K=    1
  3   243    18
H= 30, K=    1
  3   -82    58
H= 31, K=    1
  3   378    58
H=  1, K=    1
  4  1197   582
H=  2, K=    1
  4   188   187
H=  3, K=    1

  L    FO    FC
  4   233  -208
H=  4, K=    1
  4   -51    48
H=  5, K=    1
  4   -54  -131
H=  6, K=    1
  4   289   -63
H=  7, K=    1
  4   187   113
H=  8, K=    1
  4   479   473
H=  9, K=    1
  4   596   -48
H= 10, K=    1
  4   -64   -45
H= 11, K=    1
  4   753  -158
H= 12, K=    1
  4   339  -388
H= 13, K=    1
  4   754  -378
H= 14, K=    1
  4   111     3
H= 15, K=    1
  4   118   248
H= 16, K=    1
  4   -71    -8
H= 17, K=    1
  4   324   184
H= 18, K=    1
  4   118  -188
H= 19, K=    1
  4   125  -182
H= 20, K=    1
  4   139   -81
H= 21, K=    1
  4    43    73

  L    FO    FC
H= 22, K=    1
  4   -83    82
H= 23, K=    1
  4   422   175
H= 24, K=    1
  4   -88   -48
H= 25, K=    1
  4   -65   -83
H= 26, K=    1
  4   -78   -35
H= 27, K=    1
  4   181  -188
H= 28, K=    1
  4   -93    28
H= 29, K=    1
  4   -81    38
H= 30, K=    1
  4   -83    14
H=  1, K=    1
  5  1409   435
H=  2, K=    1
  5   585   408
H=  3, K=    1
  5   474  -242
H=  4, K=    1
  5   105   -72
H=  5, K=    1
  5   113    43
H=  6, K=    1
  5   402   158
H=  7, K=    1
  5   534     7
H=  8, K=    1
  5   456   213
H=  9, K=    1
  5  1032   -85
H= 10, K=    1
  5   -85  -162
  L   FO   FC
H=  11, K=   1
  5  111 -139
H=  12, K=   1
  5  -68  -57
H=  13, K=   1
  5  275 -130
H=  14, K=   1
  5  -72  150
H=  15, K=   1
  5  180    1
H=  16, K=   1
  5  146  -26
H=  17, K=   1
  5  145 -163
H=  18, K=   1
  5  293  -44
H=  19, K=   1
  5  762  191
H=  20, K=   1
  5  235  -17
H=  21, K=   1
  5  665  -41
H=  22, K=   1
  5  134   32
H=  23, K=   1
  5  517   46
H=  24, K=   1
  5  -67  153
H=  25, K=   1
  5  323  115
H=  26, K=   1
  5  -67   85
H=  27, K=   1
  5  269 -263
H=  28, K=   1
  5  157   56
H=  29, K=   1
```

```
  L   FO   FC
  5  247   28
H=   1, K=   1
  6  149  164
H=   2, K=   1
  6  289 -139
H=   3, K=   1
  6  364 -149
H=   4, K=   1
  6  269   -9
H=   5, K=   1
  6  138 -146
H=   6, K=   1
  6  559 -386
H=   7, K=   1
  6  362  166
H=   8, K=   1
  6  175  367
H=   9, K=   1
  6  329   35
H=  10, K=   1
  6  183  -76
H=  11, K=   1
  6  -71 -238
H=  12, K=   1
  6  299 -316
H=  13, K=   1
  6  -75 -166
H=  14, K=   1
  6  216  164
H=  15, K=   1
  6  256  225
H=  16, K=   1
  6  283    6
H=  17, K=   1
  6  -81  154
H=  18, K=   1
  6  -63 -266
H=  19, K=   1
```

```
  L   FO   FC
  6  321 -142
H=  20, K=   1
  6  144   11
H=  21, K=   1
  6  176   11
H=  22, K=   1
  6  139  167
H=  23, K=   1
  6  -83  165
H=  24, K=   1
  6   74 -214
H=  25, K=   1
  6  -65  -26
H=  26, K=   1
  6  171 -130
H=  27, K=   1
  6  -79  -57
H=   1, K=   1
  7  219  221
H=   2, K=   1
  7  766 -376
H=   3, K=   1
  7  534 -255
H=   4, K=   1
  7  366  173
H=   5, K=   1
  7  -71   52
H=   6, K=   1
  7  715 -144
H=   7, K=   1
  7  657  276
H=   8, K=   1
  7  145  243
H=   9, K=   1
  7  384  -46
H=  10, K=   1
  7  166    6
```

```
  L   FO   FC
H=  11, K=   1
  7  562  171
H=  12, K=   1
  7  132 -298
H=  13, K=   1
  7  439  197
H=  14, K=   1
  7  195 -161
H=  15, K=   1
  7  -82    5
H=  16, K=   1
  7  238 -262
H=  17, K=   1
  7  224  -25
H=  18, K=   1
  7  434   23
H=  19, K=   1
  7  314   -6
H=  20, K=   1
  7  166  -46
H=  21, K=   1
  7  341  -46
H=  22, K=   1
  7  128   64
H=  23, K=   1
  7  -66   25
H=  24, K=   1
  7  211  -74
H=  25, K=   1
  7  -60   21
H=   1, K=   1
  8  -77   45
H=   2, K=   1
  8  169    5
H=   3, K=   1
  8  196 -191
H=   4, K=   1
  8  244    6
```

```
   L   FO   FC
H=  5, K=  1
   0  130 -114
H=  6, K=  1
   0  191  -80
H=  7, K=  1
   0  -76   68
H=  8, K=  1
   0  208   82
H=  9, K=  1
   0  -83  -98
H= 10, K=  1
   0  -81  -28
H= 11, K=  1
   0  318 -202
H= 12, K=  1
   0  139  -83
H= 13, K=  1
   0  120 -134
H= 14, K=  1
   0  148  307
H= 15, K=  1
   0  -88   88
H= 16, K=  1
   0  -85  170
H= 17, K=  1
   0  147   97
H= 18, K=  1
   0  331 -196
H= 19, K=  1
   0  -82  -84
H= 20, K=  1
   0  -85   81
H= 21, K=  1
   0  -82  -13
H= 22, K=  1
   0  141  114
H= 23, K=  1

   L   FO   FC
   9  -89   48
H=  1, K=  1
   9  -82  -33
H=  2, K=  1
   9  -81 -140
H=  3, K=  1
   9  180  -88
H=  4, K=  1
   9  530  187
H=  5, K=  1
   9  -84  -32
H=  6, K=  1
   9  363  -41
H=  7, K=  1
   9  -83  167
H=  8, K=  1
   9  195  -87
H=  9, K=  1
   9  298 -284
H= 10, K=  1
   9  -88  -46
H= 11, K=  1
   9  236 -880
H= 12, K=  1
   9  -85   74
H= 13, K=  1
   9  -83 -113
H= 14, K=  1
   9  234   47
H= 15, K=  1
   9  -87    9
H= 16, K=  1
   9  281   65
H= 17, K=  1
   9  237  110
H= 18, K=  1
   9  196   39
H= 19, K=  1

   L   FO   FC
   9  -87  -13
H= 20, K=  1
   9  631 -181
H=  1, K=  1
  10  858  191
H=  2, K=  1
  10  -84   60
H=  3, K=  1
  10  -83 -193
H=  4, K=  1
  10  295 -107
H=  5, K=  1
  10  174   38
H=  6, K=  1
  10  -83   60
H=  7, K=  1
  10  -83   40
H=  8, K=  1
  10  -83   20
H=  9, K=  1
  10  -82   57
H= 10, K=  1
  10  -85 -121
H= 11, K=  1
  10  -83   88
H= 12, K=  1
  10  184  110
H= 13, K=  1
  10  138   10
H= 14, K=  1
  10  188  114
H= 15, K=  1
  10  -81   21
H= 16, K=  1
  10  148   82
H=  1, K=  1
  11  208   81

   L   FO   FC
H=  2, K=  1
  11  129  -57
H=  3, K=  1
  11  214   95
H=  4, K=  1
  11  -82   97
H=  5, K=  1
  11  -80 -109
H=  6, K=  1
  11  -80  119
H=  7, K=  1
  11  -88   -1
H=  8, K=  1
  11  -80  -79
H=  9, K=  1
  11  -79   57
H= 10, K=  1
  11  -77   21
H= 11, K=  1
  11  104  -42
H=  0, K=  2
   0 1366 -189
H=  2, K=  2
   0 1708  842
H=  4, K=  2
   0 1862  745
H=  6, K=  2
   0 1191 -919
H=  8, K=  2
   0 1015 -104
H= 10, K=  2
   0  746  349
H= 12, K=  2
   0 1118 -176
H= 14, K=  2
   0  241  201
H= 16, K=  2
   0  485 -489
  L   FO    FC       L   FO    FC       L   FO    FC       L   FO    FC
                     1  -84     1       1  320    45    H= 17, K=    2
H= 18, K=    2    H= 12, K=    2    H= 31, K=    2       2  346   -85
  0  657   187       1  923   -69       1  193  -130    H= 18, K=    2
H= 20, K=    2    H= 13, K=    2    H=  0, K=    2       2  242    54
  0  841   188       1  -54  -229       2 1966  -894    H= 19, K=    2
H= 22, K=    2    H= 14, K=    2    H=  1, K=    2       2  272     3
  0  444  -118       1  230  -291       2  726  -477    H= 20, K=    2
H= 24, K=    2    H= 15, K=    2    H=  2, K=    2       2  699  -224
  0  843   480       1  245   -53       2 1633   763    H= 21, K=    2
H= 26, K=    2    H= 16, K=    2    H=  3, K=    2       2  -80    34
  0  129  -232       1  128   114       2  365   288    H= 22, K=    2
H= 28, K=    2    H= 17, K=    2    H=  4, K=    2       2  592  -105
  0  325  -123       1  179  -121       2  -48   411    H= 23, K=    2
H= 30, K=    2    H= 18, K=    2    H=  5, K=    2       2  -82   134
  0  134   165       1  631   -67       2  475   314    H= 24, K=    2
H=  0, K=    2    H= 19, K=    2    H=  6, K=    2       2  147    40
  1 2825 -1448       1  415   198       2  387   173    H= 25, K=    2
H=  1, K=    2    H= 20, K=    2    H=  7, K=    2       2  293   -73
  1  -43   162       1  855  -225       2  751   -67    H= 26, K=    2
H=  2, K=    2    H= 21, K=    2    H=  8, K=    2       2  150   -95
  1 2140  -826       1  -78  -144       2  251  -398    H= 27, K=    2
H=  3, K=    2    H= 22, K=    2    H=  9, K=    2       2  187    88
  1  825  -351       1  814  -285       2  132   453    H= 28, K=    2
H=  4, K=    2    H= 23, K=    2    H= 10, K=    2       2  204    98
  1 1132  -847       1  393  -298       2 1180   320    H= 29, K=    2
H=  5, K=    2    H= 24, K=    2    H= 11, K=    2       2  127    46
  1 1222  -654       1  845  -184       2  172  -224    H= 30, K=    2
H=  6, K=    2    H= 25, K=    2    H= 12, K=    2       2  301   188
  1  644   332       1  426  -274       2  747    70    H= 31, K=    2
H=  7, K=    2    H= 26, K=    2    H= 13, K=    2       2  143   -20
  1 1021  -532       1  -87   185       2  201  -125    H=  0, K=    2
H=  8, K=    2    H= 27, K=    2    H= 14, K=    2       3  277  -852
  1  645  -256       1  124    62       2  179  -123    H=  1, K=    2
H=  9, K=    2    H= 28, K=    2    H= 15, K=    2       3 1018   851
  1  278   512       1  291   115       2  441   -55    H=  2, K=    2
H= 10, K=    2    H= 29, K=    2    H= 16, K=    2       3  942   438
  1  652  -519       1  158    23       2  -67   -10    H=  3, K=    2
H= 11, K=    2    H= 30, K=    2                          3 1887   137
```

```
   L    FO    FC
H=   4, K=   2
   3   141  -327
H=   5, K=   2
   3   211  -881
H=   6, K=   2
   3   -62   185
H=   7, K=   2
   3   835   -57
H=   8, K=   2
   3   161   227
H=   9, K=   2
   3   385  -108
H=  10, K=   2
   3   893  -382
H=  11, K=   2
   3   316   357
H=  12, K=   2
   3   -81   388
H=  13, K=   2
   3   122   282
H=  14, K=   2
   3   320  -174
H=  15, K=   2
   3   557   118
H=  16, K=   2
   3   184    11
H=  17, K=   2
   3   359   265
H=  18, K=   2
   3   290    25
H=  19, K=   2
   3   332    66
H=  20, K=   2
   3   320    28
H=  21, K=   2
   3   178   -87
H=  22, K=   2
```

```
   L    FO    FC
   3   -85   -97
H=  23, K=   2
   3   101    -4
H=  24, K=   2
   3   -85    -5
H=  25, K=   2
   3   343    53
H=  26, K=   2
   3   166   274
H=  27, K=   2
   3   464    99
H=  28, K=   2
   3   126   -44
H=  29, K=   2
   3   208    13
H=  30, K=   2
   3   108    -8
H=   0, K=   2
   4    99  -158
H=   1, K=   2
   4   294  -547
H=   2, K=   2
   4   408   344
H=   3, K=   2
   4   818    75
H=   4, K=   2
   4   201   223
H=   5, K=   2
   4  1070   108
H=   6, K=   2
   4   117   -15
H=   7, K=   2
   4   345  -371
H=   8, K=   2
   4   348  -177
H=   9, K=   2
   4   538   147
H=  10, K=   2
```

```
   L    FO    FC
   4   -83   218
H=  11, K=   2
   4   109   -47
H=  12, K=   2
   4   248   351
H=  13, K=   2
   4   493   -29
H=  14, K=   2
   4   383  -324
H=  15, K=   2
   4   344   258
H=  16, K=   2
   4   278   178
H=  17, K=   2
   4   518    38
H=  18, K=   2
   4   188   -24
H=  19, K=   2
   4   432   -73
H=  20, K=   2
   4   -81   -95
H=  21, K=   2
   4   -83    70
H=  22, K=   2
   4   318   251
H=  23, K=   2
   4   250    79
H=  24, K=   2
   4   -85   -77
H=  25, K=   2
   4   249   -71
H=  26, K=   2
   4   -85    51
H=  27, K=   2
   4   338    24
H=  28, K=   2
   4   123   -48
```

```
   L    FO    FC
H=  29, K=   2
   4   218    18
H=   0, K=   2
   5   141  -355
H=   1, K=   2
   5   143    78
H=   2, K=   2
   5   -63  -190
H=   3, K=   2
   5   282   379
H=   4, K=   2
   5   -62  -148
H=   5, K=   2
   5   748    48
H=   6, K=   2
   5   185    18
H=   7, K=   2
   5   939  -288
H=   8, K=   2
   5    63    87
H=   9, K=   2
   5   172   188
H=  10, K=   2
   5   191    14
H=  11, K=   2
   5   403   277
H=  12, K=   2
   5   131    84
H=  13, K=   2
   5   288  -108
H=  14, K=   2
   5   242   -42
H=  15, K=   2
   5   568     8
H=  16, K=   2
   5   283  -134
H=  17, K=   2
   5   888   134
```

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  L   FO    FC      L   FO    FC      L   FO    FC      L   FO    FC

H=  18, K=   2      6  321   134      6  220    60    H=  17, K=   2
  5  -62   -13    H=   8, K=   2    H=  27, K=   2      7  -85   214
H=  19, K=   2      6  122    10      6  215    -7    H=  18, K=   2
  5  245   -44    H=   9, K=   2    H=   0, K=   2      7  226  -109
H=  20, K=   2      6  234   -32      7  -74   484    H=  19, K=   2
  5  -89    11    H=  10, K=   2    H=   1, K=   2      7  -85    45
H=  21, K=   2      6  298   -75      7  160    48    H=  20, K=   2
  5  -69     4    H=  11, K=   2    H=   2, K=   2      7  248   -12
H=  22, K=   2      6  160    10      7  438   -37    H=  21, K=   2
  5  -84  -217    H=  12, K=   2    H=   3, K=   2      7  -84   -58
H=  23, K=   2      6  284   -17      7  449   190    H=  22, K=   2
  5  201   -42    H=  13, K=   2    H=   4, K=   2      7  253    29
H=  24, K=   2      6  -79  -201      7  137    39    H=  23, K=   2
  5  189    19    H=  14, K=   2    H=   5, K=   2      7  179    34
H=  25, K=   2      6  298   -97      7  223   -75    H=  24, K=   2
  5  120   205    H=  15, K=   2    H=   6, K=   2      7  170    51
H=  26, K=   2      6  344   -74      7  -75    81    H=  25, K=   2
  5  257   103    H=  16, K=   2    H=   7, K=   2      7  310   148
H=  27, K=   2      6  -82   108      7  -75  -128    H=   0, K=   2
  5  250    53    H=  17, K=   2    H=   8, K=   2      8  401   -69
H=  28, K=   2      6  148  -112      7  297    23    H=   1, K=   2
  5  -80    18    H=  18, K=   2    H=   9, K=   2      8  291   241
H=   0, K=   2      6  -84     8      7  204   119    H=   2, K=   2
  6  350  -628    H=  19, K=   2    H=  10, K=   2      8  228    37
H=   1, K=   2      6  -85  -111      7  893   407    H=   3, K=   2
  6  125    40    H=  20, K=   2    H=  11, K=   2      8  -79  -128
H=   2, K=   2      6  -87   -12      7  -81   106    H=   4, K=   2
  6  418   177    H=  21, K=   2    H=  12, K=   2      8  -80   107
H=   3, K=   2      6  -88    62      7  233   104    H=   5, K=   2
  6  463   -35    H=  22, K=   2    H=  13, K=   2      8  -79   -88
H=   4, K=   2      6  194    48      7  361   -76    H=   6, K=   2
  6  390   224    H=  23, K=   2    H=  14, K=   2      8  128  -129
H=   5, K=   2      6  173     3      7  393    33    H=   7, K=   2
  6  378   174    H=  24, K=   2    H=  15, K=   2      8  234   187
H=   6, K=   2      6  -84  -149      7  304   -48    H=   8, K=   2
  6  181  -144    H=  25, K=   2    H=  16, K=   2      8  138   -88
H=   7, K=   2      6  260     3      7  -84   -78    H=   9, K=   2
                  H=  26, K=   2                        8  259  -282
  L   FO   FC
H=  10, K=  2
  6  463  183
H=  11, K=  2
  6  -84   16
H=  12, K=  2
  6  295   44
H=  13, K=  2
  6  -83  108
H=  14, K=  2
  6  126  -21
H=  15, K=  2
  6  -86   13
H=  16, K=  2
  6  -85  -11
H=  17, K=  2
  6  -84   28
H=  18, K=  2
  6  184  -78
H=  19, K=  2
  6  -83    6
H=  20, K=  2
  6  205   12
H=  21, K=  2
  6  -83  -34
H=  22, K=  2
  6  177   19
H=   0, K=  2
  5  301  -20
H=   1, K=  2
  5  -82   45
H=   2, K=  2
  5  232  -23
H=   3, K=  2
  5  -22   37
H=   4, K=  2
  5  181   84
H=   5, K=  2

  L   FO   FC
  9  -83 -188
H=   6, K=  2
  8  137  -54
H=   7, K=  2
  9  -85   84
H=   8, K=  2
  9  126   47
H=   9, K=  2
  9  258  144
H=  10, K=  2
  9  244   43
H=  11, K=  2
  8  -85  -60
H=  12, K=  2
  9  410 -155
H=  13, K=  2
  9  232 -268
H=  14, K=  2
  9  -86   50
H=  15, K=  2
  8  284 -385
H=  16, K=  2
  9  -83   22
H=  17, K=  2
  9  -81   20
H=  18, K=  2
  9  188   36
H=  19, K=  2
  9  -79   13
H=   0, K=  2
 13  169  -12
H=   1, K=  2
 10  -82   16
H=   2, K=  2
 12  185   21
H=   3, K=  2
 13  -84  -66
H=   4, K=  2

  L   FO   FC
 13  174  186
H=   5, K=  2
 13  -82  -21
H=   6, K=  2
 13  153  -80
H=   7, K=  2
 13  234  145
H=   8, K=  2
 13  224 -128
H=   9, K=  2
 13  -83  -10
H=  10, K=  2
 13  157   -9
H=  11, K=  2
 13  -82  -45
H=  12, K=  2
 13  234 -188
H=  13, K=  2
 13  -88   34
H=  14, K=  2
 13  -79  -16
H=  15, K=  2
 13  124 -118
H=   0, K=  2
 11  183  -80
H=   1, K=  2
 11  -78   84
H=   2, K=  2
 11  113  -53
H=   3, K=  2
 11  -79  129
H=   4, K=  2
 11  -79  -31
H=   5, K=  2
 11  122    8
H=   6, K=  2
 11  -85   -7

  L   FO   FC
H=   7, K=  2
 11  153  -46
H=   8, K=  2
 11  -78   13
H=   9, K=  2
 11  -77   76
H=   2, K=  3
  0  684 1798
H=   4, K=  3
  0 1378   58
H=   6, K=  3
  0 1234  242
H=   8, K=  3
  0 1641 -403
H=  10, K=  3
  0  527  759
H=  12, K=  3
  0  712  218
H=  14, K=  3
  0  701 -232
H=  16, K=  3
  0 1346  347
H=  18, K=  3
  0  863   87
H=  20, K=  3
  0  338   78
H=  22, K=  3
  0  398 -232
H=  24, K=  3
  0  -84  473
H=  26, K=  3
  0  -87  586
H=  28, K=  3
  0  565 -148
H=  30, K=  3
  0  288   -3
H=   1, K=  3
  1  811  728
```

```
   L   FO    FC       L   FO    FC       L   FO    FC       L   FO    FC

                      1  -79   -90       2  942   147    H= 28, K=   3
H=  2, K=   1      H= 21, K=   3      H= 10, K=   3       2  -84  -243
   1  122   344       1  320   237       2  831   645    H= 29, K=   3
H=  3, K=   3      H= 22, K=   3      H= 11, K=   3       2  158    34
   1  652   522       1  218  -126       2 1280   530    H= 30, K=   3
H=  4, K=   3      H= 23, K=   3      H= 12, K=   3       2  124   -78
   1  762  -286       1  -62   -12       2  628  -229    H=  1, K=   3
H=  5, K=   3      H= 24, K=   3      H= 13, K=   3       3  414   -92
   1  338  -344       1  197   -22       2  414  -163    H=  2, K=   3
H=  6, K=   3      H= 25, K=   3      H= 14, K=   3       3  298  -494
   1  -53   340       1  -87   -38       2 1214  -539    H=  3, K=   3
H=  7, K=   3      H= 26, K=   3      H= 15, K=   3       3  285   -17
   1  234   366       1  -87    24       2  460   221    H=  4, K=   3
H=  8, K=   3      H= 27, K=   3      H= 16, K=   3       3  197  -384
   1  361   -87       1  -65   -68       2  849    29    H=  5, K=   3
H=  9, K=   3      H= 28, K=   3      H= 17, K=   3       3  280  -147
   1  246  -146       1  137   -48       2  170   -78    H=  6, K=   3
H= 10, K=   3      H= 29, K=   3      H= 18, K=   3       3  233    11
   1  320  -242       1  170  -178       2  274   218    H=  7, K=   3
H= 11, K=   3      H= 30, K=   3      H= 19, K=   3       3  -69   -85
   1  318  -155       1  -79    31       2  501  -171    H=  8, K=   3
H= 12, K=   3      H=  1, K=   3      H= 20, K=   3       3  -62  -141
   1  382   155       2  223   710       2  -82    36    H=  9, K=   3
H= 13, K=   3      H=  2, K=   3      H= 21, K=   3       3  283     0
   1  -26    41       2  740    85       2  311   180    H= 10, K=   3
H= 14, K=   3      H=  3, K=   3      H= 22, K=   3       3  -82   -81
   1  -65  -226       2 1288  -560       2  286  -355    H= 11, K=   3
H= 15, K=   3      H=  4, K=   3      H= 23, K=   3       3  -64  -213
   1  110   143       2  869  -112       2  873   110    H= 12, K=   3
H= 16, K=   3      H=  5, K=   3      H= 24, K=   3       3  -67   153
   1  139  -173       2  126   244       2  336    -1    H= 13, K=   3
H= 17, K=   3      H=  6, K=   3      H= 25, K=   3       3  811    -7
   1  -72    91       2  503  -470       2  265   -80    H= 14, K=   3
H= 18, K=   3      H=  7, K=   3      H= 26, K=   3       3  280  -146
   1  172   -57       2  301    33       2  439    43    H= 15, K=   3
H= 19, K=   3      H=  8, K=   3      H= 27, K=   3       3  137    98
   1  122    54       2  393  -257       2  191  -144    H= 16, K=   3
H= 20, K=   3      H=  9, K=   3                          3  223   -40
```

```
   L   FO    FC       L   FO    FC       L   FO    FC       L   FO    FC
H=  17, K=    3       4  511  -391       4  183   -24    H=  16, K=    3
   3  -78   -46    H=   7, K=    3    H=  26, K=    3       5  -79    18
H=  18, K=    3       4  398    82       4  -83   113    H=  17, K=    3
   3  -78    41    H=   8, K=    3    H=  27, K=    3       5  293   184
H=  19, K=    3       4  183   185       4  128  -114    H=  18, K=    3
   3  -80    54    H=   9, K=    3    H=  28, K=    3       5  -84     8
H=  20, K=    3       4 1019  -152       4  113    86    H=  19, K=    3
   3  -14   148    H=  10, K=    3    H=   1, K=    3       5  215    18
H=  21, K=    3       4  243   172       5  262   -18    H=  20, K=    3
   3  232   -87    H=  11, K=    3    H=   2, K=    3       5  -88    58
H=  22, K=    3       4 1219  -279       5  129  -144    H=  21, K=    3
   3  173  -213    H=  12, K=    3    H=   3, K=    3       5  -87   -92
H=  23, K=    3       4  237    81       5  183  -298    H=  22, K=    3
   3  -85   -15    H=  13, K=    3    H=   4, K=    3       5  178  -158
H=  24, K=    3       4  945  -278       5  -87   145    H=  23, K=    3
   3  -88  -214    H=  14, K=    3    H=   5, K=    3       5  230   183
H=  25, K=    3       4  -74  -218       5  379   334    H=  24, K=    3
   3  -24    18    H=  15, K=    3    H=   6, K=    3       5  -88   -28
H=  26, K=    3       4  -75   188       5  138  -128    H=  25, K=    3
   3  -85   -19    H=  16, K=    3    H=   7, K=    3       5  -84    18
H=  27, K=    3       4  -78  -157       5  485  -331    H=  26, K=    3
   3  -88   -93    H=  17, K=    3    H=   8, K=    3       5  -81    91
H=  28, K=    3       4  242    30       5  268  -197    H=  27, K=    3
   3  -83  -199    H=  18, K=    3    H=   9, K=    3       5  -77     4
H=  29, K=    3       4  357   157       5  417  -178    H=   1, K=    3
   3  119    28    H=  19, K=    3    H=  10, K=    3       6  546    86
H=   1, K=    3       4  410   -99       5  -71    28    H=   2, K=    3
   4 1418   342    H=  20, K=    3    H=  11, K=    3       6  316   -76
H=   2, K=    3       4  175  -117       5  299   -41    H=   3, K=    3
   4  -80   141    H=  21, K=    3    H=  12, K=    3       6  389    -1
H=   3, K=    3       4  870    92       5  285   171    H=   4, K=    3
   4  430  -275    H=  22, K=    3    H=  13, K=    3       6  587  -117
H=   4, K=    3       4  256  -108       5  482  -367    H=   5, K=    3
   4  282   388    H=  23, K=    3    H=  14, K=    3       6  210  -188
H=   5, K=    3       4  514    79       5  212   171    H=   6, K=    3
   4  -81  -114    H=  24, K=    3    H=  15, K=    3       6  558  -131
H=   6, K=    3       4  -85    93       5  -78    18    H=   7, K=    3
                   H=  25, K=    3                           6  848   358
```

```
  L   FO   FC
H=  8, K=  3
  6  160  151
H=  9, K=  3
  6  851  106
H= 10, K=  3
  6  288 -141
H= 11, K=  3
  6  366 -146
H= 12, K=  3
  6  183  146
H= 13, K=  3
  6  466  122
H= 14, K=  3
  6  -61 -105
H= 15, K=  3
  6  161  151
H= 16, K=  3
  6  -85 -287
H= 17, K=  3
  6  -67   52
H= 18, K=  3
  6  614  316
H= 19, K=  3
  6  474 -182
H= 20, K=  3
  6  -85 -114
H= 21, K=  3
  6  386  -38
H= 22, K=  3
  6  -84  -56
H= 23, K=  3
  6  121   51
H= 24, K=  3
  6  133  -58
H= 25, K=  3
  6  -86    4
H=  1, K=  3

  L   FO   FC
  7  320 -157
H=  2, K=  3
  7  -78    2
H=  3, K=  3
  7  141  -29
H=  4, K=  3
  7  132  -50
H=  5, K=  3
  7  -77    2
H=  6, K=  3
  7  158  -53
H=  7, K=  3
  7  -78 -138
H=  8, K=  3
  7  -80   44
H=  9, K=  3
  7  254  136
H= 10, K=  3
  7  -80  -17
H= 11, K=  3
  7  358  222
H= 12, K=  3
  7  201  175
H= 13, K=  3
  7  183   -7
H= 14, K=  3
  7  171   66
H= 15, K=  3
  7  -86  -46
H= 16, K=  3
  7  -86    3
H= 17, K=  3
  7  -87   45
H= 18, K=  3
  7  228  168
H= 19, K=  3
  7  171  -73
H= 20, K=  3

  L   FO   FC
  7  -84  -15
H= 21, K=  3
  7  245  137
H= 22, K=  3
  7  -82   25
H= 23, K=  3
  7  -80   87
H=  1, K=  3
  8  -83  -68
H=  2, K=  3
  8  262    2
H=  3, K=  3
  8  -82  -55
H=  4, K=  3
  8  513  127
H=  5, K=  3
  8  152 -124
H=  6, K=  3
  8  412    8
H=  7, K=  3
  8  -82   97
H=  8, K=  3
  8  -83 -214
H=  9, K=  3
  8  237 -120
H= 10, K=  3
  8  -85  -12
H= 11, K=  3
  8  420 -348
H= 12, K=  3
  8  123  220
H= 13, K=  3
  8  -80  -73
H= 14, K=  3
  8  167   82
H= 15, K=  3
  8  -86   20

  L   FO   FC
H= 16, K=  3
  8  295   57
H= 17, K=  3
  8  220   71
H= 18, K=  3
  8  232   24
H= 19, K=  3
  8  -83   11
H= 20, K=  3
  8  -86   26
H= 21, K=  3
  8  -74  -58
H=  1, K=  3
  9  -84  -34
H=  2, K=  3
  9  -83    4
H=  3, K=  3
  9  160  162
H=  4, K=  3
  9  141   14
H=  5, K=  3
  9  -84   -4
H=  6, K=  3
  9  -84 -131
H=  7, K=  3
  9  -24   37
H=  8, K=  3
  9  -84  -48
H=  9, K=  3
  9  -82   88
H= 10, K=  3
  9  -85  102
H= 11, K=  3
  9  -84  117
H= 12, K=  3
  9  -84  -20
H= 13, K=  3
  9  -83   18
  L   FO   FC
H= 14, K=  3
  9  -62   50
H= 15, K=  3
  5  -82  -58
H= 16, K=  3
  8  -80  110
H= 17, K=  3
  9  -60   75
H= 18, K=  3
  9  -77   11
H=  1, K=  3
 10  210  107
H=  2, K=  3
 10  211  -97
H=  3, K=  3
 10  -84   14
H=  4, K=  3
 10  -84   97
H=  5, K=  3
 10  -83  -40
H=  6, K=  3
 10  147   87
H=  7, K=  3
 10  -82    0
H=  8, K=  3
 10  255 -130
H=  9, K=  3
 10  -82  125
H= 10, K=  3
 10  -82   82
H= 11, K=  3
 10  -75   85
H= 12, K=  3
 10  -86   37
H= 13, K=  3
 10  -78   95
H=  1, K=  3
```

```
  L   FO   FC
 11  -76   -8
H=  2, K=  3
 11  -77   60
H=  3, K=  3
 11  -76   13
H=  4, K=  3
 11  -78  -16
H=  5, K=  3
 11  -77  -12
H=  0, K=  4
  0  938 -756
H=  2, K=  4
  0  770 -586
H=  4, K=  4
  0  -58   86
H=  6, K=  4
  0  339  373
H=  8, K=  4
  0  888 -560
H= 10, K=  4
  0  -64  -94
H= 12, K=  4
  0  316  288
H= 14, K=  4
  0  418 -486
H= 16, K=  4
  0  -74 -108
H= 18, K=  4
  0  134  -11
H= 20, K=  4
  0  -82   61
H= 22, K=  4
  0  235 -199
H= 24, K=  4
  0  -87  -57
H= 26, K=  4
  0  187  198
H= 28, K=  4
```

```
  L   FO   FC
  0  160  104
H=  0, K=  4
  1 2002 -885
H=  1, K=  4
  1  556 -372
H=  2, K=  4
  1 1031  -46
H=  3, K=  4
  1  281   71
H=  4, K=  4
  1  519  -84
H=  5, K=  4
  1   90  418
H=  6, K=  4
  1  313   79
H=  7, K=  4
  1  270   76
H=  8, K=  4
  1  971  281
H=  9, K=  4
  1  183   28
H= 10, K=  4
  1  679 -286
H= 11, K=  4
  1  -66  -61
H= 12, K=  4
  1  820   16
H= 13, K=  4
  1  141    5
H= 14, K=  4
  1  324 -108
H= 15, K=  4
  1  -73 -273
H= 16, K=  4
  1  -76  176
H= 17, K=  4
  1  238    0
```

```
  L   FO   FC
H= 18, K=  4
  1  366   12
H= 19, K=  4
  1  333  143
H= 20, K=  4
  1  765 -197
H= 21, K=  4
  1  -84  -51
H= 22, K=  4
  1  568  -79
H= 23, K=  4
  1  -84  140
H= 24, K=  4
  1  448 -154
H= 25, K=  4
  1  124   25
H= 26, K=  4
  1  -84   67
H= 27, K=  4
  1  153   28
H= 28, K=  4
  1  225   62
H= 29, K=  4
  1  -78   13
H=  0, K=  4
  2  337 -398
H=  1, K=  4
  2  -81  -17
H=  2, K=  4
  2  143 -178
H=  3, K=  4
  2  840  706
H=  4, K=  4
  2  336  295
H=  5, K=  4
  2  104   16
H=  6, K=  4
  2  340  326
```

```
    L   FO   FC
H=  7, K=   4
  2  -88 -143
H=  8, K=   4
  2  268 -238
H=  9, K=   4
  2  424  349
H= 10, K=   4
  2  175  211
H= 11, K=   4
  2  -67   36
H= 12, K=   4
  2  430  467
H= 13, K=   4
  2  -73   -1
H= 14, K=   4
  4  147  -75
H= 15, K=   4
  2  -73   60
H= 16, K=   4
  2  136 -139
H= 17, K=   4
  2  100  268
H= 18, K=   4
  2  -80   19
H= 19, K=   4
  2  208 -124
H= 20, K=   4
  2  -84  106
H= 21, K=   4
  2  -24   12
H= 22, K=   4
  2  140 -141
H= 23, K=   4
  2  245  249
H= 24, K=   4
  2  -65 -169
H= 25, K=   4
```

```
    L   FC   FC
  2  168  138
H= 26, K=   4
  2  -85  132
H= 27, K=   4
  2  152  144
H= 28, K=   4
  2  124  144
H=  0, K=   4
  3  771  219
H=  1, K=   4
  3   95 -198
H=  2, K=   4
  3 1001  637
H=  3, K=   4
  3  672   -7
H=  4, K=   4
  3  246   58
H=  5, K=   4
  3 1133  289
H=  6, K=   4
  3  203  -48
H=  7, K=   4
  3  596 -170
H=  8, K=   4
  3  263  128
H=  9, K=   4
  3  233 -158
H= 10, K=   4
  3  449  -11
H= 11, K=   4
  3  -73   65
H= 12, K=   4
  3  158  158
H= 13, K=   4
  3  428    8
H= 14, K=   4
  3  335 -203
H= 15, K=   4
```

```
    L   FO   FC
  3  455  144
H= 16, K=   4
  3  377  287
H= 17, K=   4
  3  634  -58
H= 18, K=   4
  3  278   36
H= 19, K=   4
  3  384  -21
H= 20, K=   4
  3  230  -49
H= 21, K=   4
  3  -85   57
H= 22, K=   4
  3  567  311
H= 23, K=   4
  3  158  -41
H= 24, K=   4
  3  -85  -41
H= 25, K=   4
  3  375   92
H= 26, K=   4
  3  -21   27
H= 27, K=   4
  3  269  -20
H= 28, K=   4
  3  203 -115
H=  0, K=   4
  4  -66  -57
H=  1, K=   4
  4  433  413
H=  2, K=   4
  4  247  186
H=  3, K=   4
  4  288  330
H=  4, K=   4
  4  -67   12
```

```
    L   FO   FC
H=  5, K=   4
  4  435 -219
H=  6, K=   4
  4  210 -194
H=  7, K=   4
  4  112   67
H=  8, K=   4
  4  120  151
H=  9, K=   4
  4  -73  140
H= 10, K=   4
  4  -72    0
H= 11, K=   4
  4  -76    9
H= 12, K=   4
  4  134  229
H= 13, K=   4
  4  -77 -133
H= 14, K=   4
  4  160  137
H= 15, K=   4
  4  -78 -172
H= 16, K=   4
  4  388 -307
H= 17, K=   4
  4  498  328
H= 18, K=   4
  4  -83  -28
H= 19, K=   4
  4  -85 -118
H= 20, K=   4
  4  187  177
H= 21, K=   4
  4  121 -118
H= 22, K=   4
  4  -84  -23
H= 23, K=   4
  4  103  104
```

```
 L    FO    FC      L    FO    FC      L    FO    FC      L    FO    FC

H=  24, K=   4      5   232   -91      6   -77   -28    H=   1, K=   4
  4   -86   -53   H=  15, K=   4    H=   8, K=   4      7   148    51
H=  25, K=   4      5   374  -149      6   337   241    H=   2, K=   4
  4   -83    11   H=  16, K=   4    H=   9, K=   4      7   337   -11
H=  26, K=   4      5   -84   163      6   311   308    H=   3, K=   4
  4   -98    26   H=  17, K=   4    H=  10, K=   4      7   177   -84
H=  27, K=   4      5   337  -143      6   -83   -93    H=   4, K=   4
  4   -76    16   H=  18, K=   4    H=  11, K=   4      7   198   -38
H=   0, K=   4      5   -85    13      6   -82    44    H=   5, K=   4
  5   -71  -166   H=  19, K=   4    H=  12, K=   4      7   284   -92
H=   1, K=   4      5   148   -81      6   -83    13    H=   6, K=   4
  5   -71   242   H=  20, K=   4    H=  13, K=   4      7   -61  -129
H=   2, K=   4      5   -66   -46      6   418  -418    H=   7, K=   4
  5   -73   -34   H=  21, K=   4    H=  14, K=   4      7   234    49
H=   3, K=   4      5   -68    22      6   329   261    H=   8, K=   4
  5   767  -129   H=  22, K=   4    H=  15, K=   4      7   185    -2
H=   4, K=   4      5   164     2      6   176  -133    H=   9, K=   4
  5   167    -8   H=  23, K=   4    H=  16, K=   4      7   145  -138
H=   5, K=   4      5   255   -56      6   172  -176    H=  10, K=   4
  5   872    89   H=  24, K=   4    H=  17, K=   4      7   441   148
H=   6, K=   4      5   127   -38      6   -86    76    H=  11, K=   4
  5   -78   -79   H=  25, K=   4    H=  18, K=   4      7   129   -37
H=   7, K=   4      5   188    14      6   -85   -12    H=  12, K=   4
  5   310   262   H=   0, K=   4    H=  19, K=   4      7   218   -78
H=   8, K=   4      6   -74   183      6   -25    -8    H=  13, K=   4
  5   -76   -34   H=   1, K=   4    H=  20, K=   4      7   -64   219
H=   9, K=   4      6   146   182      6   129   136    H=  14, K=   4
  5   963  -234   H=   2, K=   4    H=  21, K=   4      7   316    88
H=  10, K=   4      6   -77   139      6   -85   -13    H=  15, K=   4
  5   148   -76   H=   3, K=   4    H=  22, K=   4      7   -68   144
H=  11, K=   4      6   175   153      6   -61     3    H=  16, K=   4
  5   -78     0   H=   4, K=   4    H=  23, K=   4      7   -85   -82
H=  12, K=   4      6   132    21      6   -83   -35    H=  17, K=   4
  5   381  -218   H=   5, K=   4    H=  24, K=   4      7   153    37
H=  13, K=   4      6   -77  -124      6   -79   -63    H=  18, K=   4
  5   322   -78   H=   6, K=   4    H=   0, K=   4      7   -86   -26
H=  14, K=   4      6   -77    -4      7   133   243    H=  19, K=   4
                  H=   7, K=   4                           7   -64     8
  L   FC     FC       L   FO     FC       L   FO     FC       L   FO     FC
H= 20, K=   4        8  -83     -5        9  122    -12      H= 14, K=   5
  7  160     41     H= 16, K=   4       H= 15, K=   4          0  703    228
H= 21, K=   4        8  -83     45        9   79    -35      H= 16, K=   5
  7  125     25     H= 17, K=   4       H=  0, K=   4          0  611     84
H= 22, K=   4        8  -82    -84       10  104    193      H= 18, K=   5
  7  221    -49     H= 18, K=   4       H=  1, K=   4          0  158   -499
H=  0, K=   4        8  132    -75       10  -81    124      H= 20, K=   5
  8  228    154     H= 19, K=   4       H=  2, K=   4          0  232     98
H=  1, K=   4        8  -70     30       10  -79    -45      H= 22, K=   5
  8  -24     30     H=  0, K=   4       H=  3, K=   4          0  -85     19
H=  2, K=   4        9  420    141       10  -80     55      H= 24, K=   5
  8  -82   -119     H=  1, K=   4       H=  4, K=   4          0  473   -233
H=  3, K=   4        9  102   -158       10  110   -100      H= 26, K=   5
  8  -24     20     H=  2, K=   4       H=  5, K=   4          0  231     29
H=  4, K=   4        9  152    -70       10  -78    -20      H=  1, K=   5
  8  184   -122     H=  3, K=   4       H=  6, K=   4          1  104    -19
H=  5, K=   4        9  -83    -84       10  -78     71      H=  2, K=   5
  8  -83    -79     H=  4, K=   4       H=  7, K=   4          1  -67   -117
H=  6, K=   4        9  -84    -18       10  -78     20      H=  3, K=   5
  8  -65     98     H=  5, K=   4       H=  8, K=   4          1  125    220
H=  7, K=   4        9  -83     -9       10  -78     -8      H=  4, K=   5
  8  -84   -158     H=  6, K=   4       H=  9, K=   4          1  340    -65
H=  8, K=   4        9  -83     72       10  -77     -6      H=  5, K=   5
  8  -83     21     H=  7, K=   4       H= 10, K=   4          1  -67     21
H=  9, K=   4        9  -84     48       10  156   -183      H=  6, K=   5
  8  171    147     H=  8, K=   4       H=  2, K=   5          1  272    -70
H= 10, K=   4        9  238    -72        0  274    122      H=  7, K=   5
  8  280   -105     H=  9, K=   4       H=  4, K=   5          1  -68    -68
H= 11, K=   4        9  123    104        0  646   -245      H=  8, K=   5
  8  -84    -15     H= 10, K=   4       H=  6, K=   5          1  423    170
H= 12, K=   4        9  307    -70        0  512    188      H=  9, K=   5
  8  224   -147     H= 11, K=   4       H=  8, K=   5          1  -71   -112
H= 13, K=   4        9  -81    -78        0  523    -70      H= 10, K=   5
  8  282   -280     H= 12, K=   4       H= 10, K=   5          1  -73    -80
H= 14, K=   4        9  273   -100        0  208   -108      H= 11, K=   5
  8  -84    110     H= 13, K=   4       H= 12, K=   5          1  402    273
H= 15, K=   4        9  -80     13        0  104    -25      H= 12, K=   5
                    H= 14, K=   4                                1  218   -131
  L   FO   FC
H=  13, K=   5
  1  243  123
H=  14, K=   5
  1  365 -167
H=  15, K=   5
  1  -79  -41
H=  16, K=   5
  1  422 -190
H=  17, K=   5
  1  246 -232
H=  18, K=   5
  1  207  -30
H=  19, K=   5
  1  -84  -20
H=  20, K=   5
  1  -44   -6
H=  21, K=   5
  1  213  320
H=  22, K=   5
  1  -84  -72
H=  23, K=   5
  1  150  -78
H=  24, K=   5
  1  -85 -163
H=  25, K=   5
  1  131 -136
H=  26, K=   5
  1  -80  -57
H=  27, K=   5
  1  -78   59
H=   1, K=   5
  2  782 -293
H=   2, K=   5
  2  024 -110
H=   3, K=   5
  2  576 -250
H=   4, K=   5

  L   FO   FC
  2  974 -729
H=   5, K=   5
  2  184  122
H=   6, K=   5
  2  568   61
H=   7, K=   5
  2  -70 -163
H=   8, K=   5
  2  457  108
H=   9, K=   5
  2  408   56
H=  10, K=   5
  2  244 -270
H=  11, K=   5
  2  352  -68
H=  12, K=   5
  2  -70   83
H=  13, K=   5
  2  461  138
H=  14, K=   5
  2  195  180
H=  15, K=   5
  2  -81  -79
H=  16, K=   5
  2  325   52
H=  17, K=   5
  2  330 -251
H=  18, K=   5
  2  322  -66
H=  19, K=   5
  2  -85  181
H=  20, K=   5
  2  -86   77
H=  21, K=   5
  2  397 -216
H=  22, K=   5
  2  -86   38
H=  23, K=   5

  L   FO   FC
  2  243  -82
H=  24, K=   5
  2 [illegible] -250
H=  25, K=   5
  2   82  115
H=  26, K=   5
  2  129 -234
H=   1, K=   5
  3  -70 -320
H=   2, K=   5
  3  -71   19
H=   3, K=   5
  3  871   74
H=   4, K=   5
  3  241 -118
H=   5, K=   5
  3  175  125
H=   6, K=   5
  3  188   -8
H=   7, K=   5
  3  289  -82
H=   8, K=   5
  3  231  280
H=   9, K=   5
  3  449 -261
H=  10, K=   5
  3  182 -155
H=  11, K=   5
  3  331  -48
H=  12, K=   5
  3  182  104
H=  13, K=   5
  3  -82  106
H=  14, K=   5
  3  -82   18
H=  15, K=   5
  3  125  -39

  L   FO   FC
H=  16, K=   5
  3  -84 -182
H=  17, K=   5
  3  -86 -147
H=  18, K=   5
  3  211  154
H=  19, K=   5
  3  178   45
H=  20, K=   5
  3  -87   80
H=  21, K=   5
  3  192   82
H=  22, K=   5
  3  -83   32
H=  23, K=   5
  3  -84 -128
H=  24, K=   5
  3  -82  -85
H=  25, K=   5
  3  -88  -90
H=  26, K=   5
  3  -77   54
H=   1, K=   5
  4  367 -152
H=   2, K=   5
  4  -74   14
H=   3, K=   5
  4  288  -81
H=   4, K=   5
  4  176  284
H=   5, K=   5
  4  182  131
H=   6, K=   5
  4  187  -92
H=   7, K=   5
  4  342 -180
H=   8, K=   5
  4  -70   70
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   L   FO   FC       L   FO   FC       L   FO   FC       L   FO   FC
H=  9, K=   5        5  -76  128       5  -85  -14    H= 17, K=   5
   4  555  -91    H=  3, K=   5     H= 22, K=   5        6  145  -22
H= 10, K=   5        5  -78   94       5  -83  -34    H= 18, K=   5
   4  -78  -47    H=  4, K=   5     H= 23, K=   5        6  150  -24
H= 11, K=   5        5  224 -144       5  139  -49    H= 19, K=   5
   4  575 -102    H=  5, K=   5     H=  1, K=   5        6  200 -119
H= 12, K=   5        5  249  274       6  416  -62    H= 20, K=   5
   4  165   66    H=  6, K=   5     H=  2, K=   5        6  -62   42
H= 13, K=   5        5  139  -16       6  336 -276    H= 21, K=   5
   4  240   92    H=  7, K=   5     H=  3, K=   5        6  207   15
H= 14, K=   5        5  135   31       6  229  -12    H=  1, K=   5
   4  434  348    H=  8, K=   5     H=  4, K=   5        7  -63  -66
H= 15, K=   5        5  123   26       6  122  208    H=  2, K=   5
   4  274 -155    H=  9, K=   5     H=  5, K=   5        7  146   53
H= 16, K=   5        5  -87 -131       6  -71   76    H=  3, K=   5
   4  176   89    H= 10, K=   5     H=  6, K=   5        7  -84 -118
H= 17, K=   5        5  296 -177       6  329 -158    H=  4, K=   5
   4  -55 -167    H= 11, K=   5     H=  7, K=   5        7  257  127
H= 18, K=   5        5  -65  -21       6  255   62    H=  5, K=   5
   4  -56  -17    H= 12, K=   5     H=  8, K=   5        7  -83   93
H= 19, K=   5        5  -53   91       6  -53   66    H=  6, K=   5
   4  487  237    H= 13, K=   5     H=  9, K=   5        7  -85    5
H= 20, K=   5        5  320  285       6  349   71    H=  7, K=   5
   4  124  -66    H= 14, K=   5     H= 10, K=   5        7  -84  -89
H= 21, K=   5        5  -84   -4       6  -64  217    H=  8, K=   5
   4  173 -128    H= 15, K=   5     H= 11, K=   5        7  -83 -116
H= 22, K=   5        5  -85  -50       6  656  418    H=  9, K=   5
   4  -55  139    H= 16, K=   5     H= 12, K=   5        7  225 -174
H= 23, K=   5        5  -87 -133       6  219 -235    H= 10, K=   5
   4  -83  -73    H= 17, K=   5     H= 13, K=   5        7  136   47
H= 24, K=   5        5  -85  -46       6  346  169    H= 11, K=   5
   4  -80  101    H= 18, K=   5     H= 14, K=   5        7  -83   25
H= 25, K=   5        5  -84  -91       6  -87   45    H= 12, K=   5
   4  157  132    H= 19, K=   5     H= 15, K=   5        7  -84   61
H=  1, K=   5        5  -85  189       6  -86 -139    H= 13, K=   5
   5  315  -65    H= 20, K=   5     H= 16, K=   5        7  -84  113
H=  2, K=   5        5  -84   -9       6  152   32    H= 14, K=   5
                  H= 21, K=   5                          7  -84  104
   L   FO    FC        L   FO    FC        L   FO    FC        L   FO    FC

                       8  238   -77                          H=  11, K=   6
H=  15, K=   5       H=  15, K=   5        0  -78  -370        1  -81  -103
   7  177  -162        8  -80   -16      H=  12, K=   6      H=  12, K=   6
H=  16, K=   5       H=  16, K=   5        0  378    56        1  348   183
   7  -42    62        8  146    51      H=  14, K=   6      H=  13, K=   6
H=  17, K=   5       H=   1, K=   5        0  -82  -119        1  138    42
   7  -81   -88        9  136   102      H=  16, K=   6      H=  14, K=   6
H=  18, K=   5       H=   2, K=   5        0  -84    -5        1  211   135
   7  150   -84        9  -81   -63      H=  18, K=   6      H=  15, K=   6
H=  19, K=   5       H=   3, K=   5        0  -85   232        1  -84    -8
   7  118   101        9  -82    65      H=  20, K=   6      H=  16, K=   6
H=   1, K=   5       H=   4, K=   5        0  211   -12        1  -84    -8
   8  -83   -57        9  -83    57      H=  22, K=   6      H=  17, K=   6
H=   2, K=   5       H=   5, K=   5        0  347  -142        1  185   184
   8  219   117        9  -81    32      H=  24, K=   6      H=  18, K=   6
H=   3, K=   5       H=   6, K=   5        0  -81     0        1  173    12
   8  162   159        9  -81   -11      H=   0, K=   6      H=  19, K=   6
H=   4, K=   5       H=   7, K=   5        1  -79   238        1  -86  -124
   8  177   -34        9  -79   -18      H=   1, K=   6      H=  20, K=   6
H=   5, K=   5       H=   8, K=   5        1  -77   -53        1  193   -43
   8  -83    25        9  115   -98      H=   2, K=   6      H=  21, K=   6
H=   6, K=   5       H=   9, K=   5        1  141   152        1  -84   -36
   8  238    22        9  -79    -4      H=   3, K=   6      H=  22, K=   6
H=   7, K=   5       H=  10, K=   5        1  267   361        1  188    17
   8  -82    28        9  -77    62      H=   4, K=   6      H=  23, K=   6
H=   8, K=   5       H=  11, K=   5        1  -78    85        1  188   271
   8  -84   -28        9  -77   181      H=   5, K=   6      H=  24, K=   6
H=   9, K=   5       H=   0, K=   6        1  181   -29        1  179   -78
   8  124   -28        0  887  -240      H=   6, K=   6      H=   0, K=   6
H=  10, K=   5       H=   2, K=   6        1  -78   -33        2  434   156
   8  -83    -6        0  281    67      H=   7, K=   6      H=   1, K=   6
H=  11, K=   5       H=   4, K=   6        1  137   -21        2  -77   -39
   8  -83    61        0  -78    38      H=   8, K=   6      H=   2, K=   6
H=  12, K=   5       H=   6, K=   6        1  515   307        2  525   207
   8  -83   -19        0  146    79      H=   9, K=   6      H=   3, K=   6
H=  13, K=   5       H=   8, K=   6        1  147   206        2  248    24
   8  -81   -66        0  177  -105      H=  10, K=   6      H=   4, K=   6
H=  14, K=   5       H=  10, K=   6        1  385    11        2  238   163
```

```
 L   FO    FC
H=  5, K=  6
  2  348   78
H=  6, K=  6
  2  -76   25
H=  7, K=  6
  2  125 -121
H=  8, K=  6
  1  238  -40
H=  9, K=  6
  2  -81 -141
H= 10, K=  6
  2  217   -8
H= 11, K=  6
  2  116  162
H= 12, K=  6
  2  -62  101
H= 13, K=  6
  2  -24   -2
H= 14, K=  6
  2  140  -16
H= 15, K=  6
  2  201  -22
H= 16, K=  6
  2  -63   -1
H= 17, K=  6
  2  -84   23
H= 18, K=  6
  2  268  162
H= 19, K=  6
  2  164 -128
H= 20, K=  6
  2  226   24
H= 21, K=  6
  2  -84  -27
H= 22, K=  6
  2  -64    2
H= 23, K=  6

  2  -81    9
H= 24, K=  6
  2  -86   63
H=  0, K=  6
  3  338  160
H=  1, K=  6
  3  214  112
H=  2, K=  6
  3  517  154
H=  3, K=  6
  3  145  -65
H=  4, K=  6
  3  -79  -36
H=  5, K=  6
  3  -66 -142
H=  6, K=  6
  3  321 -276
H=  7, K=  6
  3  274   25
H=  8, K=  6
  3  -61  158
H=  9, K=  6
  3  167   17
H= 10, K=  6
  3  219  -71
H= 11, K=  6
  3  -64  -26
H= 12, K=  6
  3  -63   47
H= 13, K=  6
  3  254 -146
H= 14, K=  6
  3  122   65
H= 15, K=  6
  3  106   56
H= 16, K=  6
  3  -67 -118
H= 17, K=  6

 L   FO    FC
  3  -86   46
H= 18, K=  6
  3  -83  -44
H= 19, K=  6
  3  186  -72
H= 20, K=  6
  3  177   45
H= 21, K=  6
  3  -82    6
H= 22, K=  6
  3  263  247
H= 23, K=  6
  3  -76  -21
H=  0, K=  6
  4  119 -125
H=  1, K=  6
  4  419 -366
H=  2, K=  6
  4  143 -161
H=  3, K=  6
  4  215   16
H=  4, K=  6
  4  -81   38
H=  5, K=  6
  4  173  121
H=  6, K=  6
  4  -82 -174
H=  7, K=  6
  4  625  357
H=  8, K=  6
  4  217 -288
H=  9, K=  6
  4  152   75
H= 10, K=  6
  4  -64  111
H= 11, K=  6
  4  166  125

          FC
H= 12, K=  6
  4  161 -143
H= 13, K=  6
  4  -85 -161
H= 14, K=  6
  4  163 -148
H= 15, K=  6
  4  231   33
H= 16, K=  6
  4  -65   29
H= 17, K=  6
  4  256   47
H= 18, K=  6
  4  -64  -27
H= 19, K=  6
  4  -62  -54
H= 20, K=  6
  4  -62  -24
H= 21, K=  6
  4  -61  -52
H= 22, K=  6
  4  -77   11
H=  0, K=  6
  5  -62  -23
H=  1, K=  6
  5  -64  165
H=  2, K=  6
  5  -63  -66
H=  3, K=  6
  5  311 -142
H=  4, K=  6
  5  -64   71
H=  5, K=  6
  5  218  -24
H=  6, K=  6
  5  -62   71
H=  7, K=  6
  6  -63  179
 L    FO    FC
H=  8, K=    6
  5  -82    -7
H=  9, K=    6
  5  -64    67
H= 10, K=    6
  5  -88  -102
H= 11, K=    6
  5  -84    -5
H= 12, K=    6
  5  137  -119
H= 13, K=    6
  5  -86   -28
H= 14, K=    6
  5  12[illegible]   64
H= 15, K=    6
  5  157   -30
H= 16, K=    6
  5  172    63
H= 17, K=    6
  5  -82  -141
H= 18, K=    6
  5  -82    -2
H= 19, K=    6
  5  -76    -1
H= 20, K=    6
  5  -75    12
H=  0, K=    6
  6  241    -[illegible]
H=  1, K=    6
  6  -88    -2
H=  2, K=    6
  6  -88    33
H=  3, K=    6
  6  -84   -28
H=  4, K=    6
  6  -85   186
H=  5, K=    6
```

```
 L    FO    FC
  6  -86   -66
H=  6, K=    6
  6  126  -164
H=  7, K=    6
  6  -84   -16
H=  8, K=    6
  6  -83   -66
H=  9, K=    6
  6  -86    22
H= 10, K=    6
  6  422   678
H= 11, K=    6
  6  -83   116
H= 12, K=    6
  6  -84   -57
H= 13, K=    6
  6  -84    64
H= 14, K=    6
  6  -87   -44
H= 15, K=    6
  6  131   -16
H= 16, K=    6
  6  -82    62
H= 17, K=    6
  6  -86   175
H= 18, K=    6
  6  116   -74
H=  0, K=    6
  7  -83     6
H=  1, K=    6
  7  -83    36
H=  2, K=    6
  7  182  -107
H=  3, K=    6
  7  -84   -32
H=  4, K=    6
  7  -83    -6
H=  5, K=    6
```

```
 L    FO    FC
  7  -83   -36
H=  6, K=    6
  7  -83    15
H=  7, K=    6
  7  -82   -95
H=  8, K=    6
  7  -82   -46
H=  9, K=    6
  7  -83   -36
H= 10, K=    6
  7  -82   -52
H= 11, K=    6
  7  -82   -46
H= 12, K=    6
  7  -81   -63
H= 13, K=    6
  7  -86    68
H= 14, K=    6
  7  -79    68
H= 15, K=    6
  7  -78   166
H=  0, K=    6
  8  -82  -275
H=  1, K=    6
  8  -81   134
H=  2, K=    6
  8  147    36
H=  3, K=    6
  8  -83   -66
H=  4, K=    6
  8  142   123
H=  5, K=    6
  8  128  -171
H=  6, K=    6
  8  147  -168
H=  7, K=    6
  8  136   114
```

```
 L    FO    FC
H=  8, K=    6
  8  -76    60
H=  9, K=    6
  8  -77    -4
H= 10, K=    6
  8   79    74
H= 11, K=    6
  8  -76     7
H=  0, K=    6
  9  151    64
H=  1, K=    6
  9  -76   -21
H=  2, K=    6
  9  -78   -26
H=  2, K=    7
  0  377  -323
H=  4, K=    7
  0  -62    27
H=  6, K=    7
  0  302   516
H=  8, K=    7
  0   84   -62
H= 10, K=    7
  0  311  -323
H= 12, K=    7
  0  268   121
H= 14, K=    7
  0  -65   -91
H= 16, K=    7
  0  -66  -228
H= 18, K=    7
  0  -72  -128
H= 20, K=    7
  0  -76    61
H=  1, K=    7
  1  371  -268
H=  2, K=    7
  1  132    -7
  L    FO    FC       L    FO    FC       L    FO    FC       L    FO    FC
                      1   144  -132                          H= 18, K=     7
H=  3, K=     7                           2   -81    43
                    H=  1, K=     7                           3   -81    58
  1   -84   138                         H= 20, K=     7
                      2   196  -115                          H= 19, K=     7
H=  4, K=     7                           2   184   179
                    H=  2, K=     7                           3   -79  -101
  1   230   -33                         H=  1, K=     7
                      2   382  -464                          H=  1, K=     7
H=  5, K=     7                           3   228     7
                    H=  3, K=     7                           4   -85     4
  1   178  -131                         H=  2, K=     7
                      2   164  -148                          H=  2, K=     7
H=  6, K=     7                           3   204   288
                    H=  4, K=     7                           4   138   -85
  1   198   -92                         H=  3, K=     7
                      2   102    75                          H=  3, K=     7
H=  7, K=     7                           3   168   -38
                    H=  5, K=     7                           4   168   117
  1   164  -163                         H=  4, K=     7
                      2   349   364                          H=  4, K=     7
H=  8, K=     7                           3   -82   103
                    H=  6, K=     7                           4   127   204
  1   335   152                         H=  5, K=     7
                      2   341   288                          H=  5, K=     7
H=  9, K=     7                           3   -82    44
                    H=  7, K=     7                           4   244   285
  1   388   303                         H=  6, K=     7
                      2   142  -215                          H=  6, K=     7
H= 10, K=     7                           3   -88   -52
                    H=  8, K=     7                           4   -84   138
  1   -83    14                         H=  7, K=     7
                      2   -83   -83                          H=  7, K=     7
H= 11, K=     7                           3   -84    -1
                    H=  9, K=     7                           4   253  -214
  1   -83   -57                         H=  8, K=     7
                      2   -84   -43                          H=  8, K=     7
H= 12, K=     7                           3   141   284
                    H= 10, K=     7                           4   142  -151
  1   188  -181                         H=  9, K=     7
                      2   -85  -183                          H=  9, K=     7
H= 13, K=     7                           3   153    57
                    H= 11, K=     7                               143   -48
  1   -86  -112                         H= 10, K=     7
                      2   128    72                          H= 10, K=     7
H= 14, K=     7                           3   -81     2
                    H= 12, K=     7                           4 [illegible] -202
  1   -86    26                         H= 11, K=     7
                      2   130   107                          H= 11, K=     7
H= 15, K=     7                           3   -85   108
                    H= 13, K=     7                           4   -84    73
  1   -48    34                         H= 12, K=     7
                      2   -85  -113                          H= 12, K=     7
H= 16, K=     7                           3   -87   -54
                    H= 14, K=     7                           4   -83    85
  1   263   -62                         H= 13, K=     7
                      2   -88   127                          H= 13, K=     7
H= 17, K=     7                           3   280  -131
                    H= 15, K=     7                           4   152   -65
  1   -83   -32                         H= 14, K=     7
                      2   -83    38                          H= 14, K=     7
H= 18, K=     7                           3   383   188
                    H= 16, K=     7                           4   184   157
  1   -85    25                         H= 15, K=     7
                      2   -86   -44                          H= 15, K=     7
H= 19, K=     7                           1   -85    -1
                    H= 17, K=     7                           4   -81   -53
  1   -83   -48                         H= 16, K=     7
                      2   -84    81                          H= 16, K=     7
H= 20, K=     7                           3   -83     0
                    H= 18, K=     7                           4   -81  -182
  1   -86    41                         H= 17, K=     7
                      2   -82   -17                          H= 17, K=     7
H= 21, K=     7                           3   157   138
                    H= 19, K=     7                           4   -79   112
  L    FO    FC
H=  10, K=   7
  4   -78  -115
H=   1, K=   7
  5   -21   114
H=   2, K=   7
  5   -64    56
H=   3, K=   7
  5   121    -4
H=   4, K=   7
  5   145   -46
H=   5, K=   7
  5   -84   -12
H=   6, K=   7
  5   -84   -67
H=   7, K=   7
  5   202   185
H=   8, K=   7
  5 [illegible] 133
H=   9, K=   7
  5   211    64
H=  10, K=   7
  5   -85    25
H=  11, K=   7
  5   266   188
H=  12, K=   7
  5   171  -184
H=  13, K=   7
  5   157    81
H=  14, K=   7
  5   -81   -86
H=  15, K=   7
  5   -80   -83
H=  16, K=   7
  5   -77   -66
H=   1, K=   7
  6   100  -110
H=   2, K=   7

  L    FO    FC
  6    81   -82
H=   3, K=   7
  6   -82   127
H=   4, K=   7
  6   -83   -44
H=   5, K=   7
  6   155  -132
H=   6, K=   7
  6   -82   111
H=   7, K=   7
  6   130  -136
H=   8, K=   7
  6   -82    -1
H=   9, K=   7
  6   -83     8
H=  10, K=   7
  6   -81   -79
H=  11, K=   7
  6   103   118
H=  12, K=   7
  6   -88    87
H=  13, K=   7
  6   151    96
H=   1, K=   7
  7   140    80
H=   2, K=   7
  7   120    72
H=   3, K=   7
  7   -81  -125
H=   4, K=   7
  7   128    31
H=   5, K=   7
  7   -80   -14
H=   6, K=   7
  7   113     9
H=   7, K=   7
  7   -70    68
H=   8, K=   7

  L    FO    FC
  7   -71   -43
H=   9, K=   7
  7   184  -115
H=   0, K=   8
  0    85   383
H=   2, K=   8
  0   257   -94
H=   4, K=   8
  0   292  -234
H=   6, K=   8
  0   247   238
H=   8, K=   8
  0   242   116
H=  10, K=   8
  0   -83   -91
H=  12, K=   8
  0   280    85
H=  14, K=   8
  0   -82     1
H=  16, K=   8
  0   -78    98
H=   0, K=   8
  1   -85    85
H=   1, K=   8
  1 [illegible] -107
H=   2, K=   8
  1   -86   -61
H=   3, K=   8
  1   -84   -34
H=   4, K=   8
  1   -81    -3
H=   5, K=   8
  1   124    46
H=   6, K=   8
  1   -85   111
H=   7, K=   8
  1   -84   -73

  L    FO    FC
H=   8, K=   8
  1   -82     2
H=   9, K=   8
  1   -84   -86
H=  10, K=   8
  1   -85   117
H=  11, K=   8
  1   -83  -109
H=  12, K=   8
  1   131   130
H=  13, K=   8
  1   -84   173
H=  14, K=   8
  1   -79     1
H=  15, K=   8
  1   112   102
H=  16, K=   8
  1   -77    11
H=   0, K=   8
  2   469   343
H=   1, K=   8
  2   -84   -47
H=   2, K=   8
  2 [illegible] 54
H=   3, K=   8
  2   -85  -219
H=   4, K=   8
  2   139  -170
H=   5, K=   8
  2   281   182
H=   6, K=   8
  2   -84    30
H=   7, K=   8
  2   129    28
H=   8, K=   8
  2   -82   104
H=   9, K=   8
  2   -83  -110
```

```
   L   FO    FC     L   FO    FC     L   FO    FC     L   FO    FC

H= 10, K=    8   H= 11, K=    8   H=  0, K=    8   H=  0, K=    9
   2  216   -81     3  -81     4     5  -88   -78     0  -78    77
H= 11, K=    8   H= 12, K=    8   H=  1, K=    8   H=  1, K=    9
   2  -83    67     3  -78    35     5  -88   -41     1  -78    60
H= 12, K=    8   H= 13, K=    8   H=  2, K=    8   H=  2, K=    9
   2  -81   -10     3  113    82     5  -83    -7     1  -78   -31
H= 13, K=    8   H= 14, K=    8   H=  3, K=    8   H=  3, K=    9
   2  142  -101     3  -77   -62     5  122  -112     1  140  -161
H= 14, K=    8   H=  0, K=    8   H=  4, K=    8   H=  4, K=    9
   2  -75    87     4  -84  -139     5  -83    74     1  -79   -31
H= 15, K=    8   H=  1, K=    8   H=  5, K=    8   H=  5, K=    9
   2  -78    20     4  -83   -44     5   40   147     1  126   145
H=  0, K=    8   H=  2, K=    8   H=  6, K=    8   H=  6, K=    9
   3  -64   -28     4  151   -96     5  -80    82     1  -78   -42
H=  1, K=    8   H=  3, K=    8   H=  7, K=    8   H=  7, K=    9
   3  -64  -127     4  262  -187     5  -79   130     1  -78   -11
H=  2, K=    8   H=  4, K=    8   H=  8, K=    8   H=  8, K=    9
   3  -84  -107     4  131   -38     5  -79    88     1  -78    -8
H=  3, K=    8   H=  5, K=    8   H=  9, K=    8   H=  1, K=    9
   3  159  -178     4  -88   137     5  -77   -85     2  -78    33
H=  4, K=    8   H=  6, K=    8   H=  0, K=    8   H=  2, K=    9
   3  -84  -148     4  -83    33     6  -75    -9     2  105   107
H=  5, K=    8   H=  7, K=    8   H=  1, K=    8   H=  3, K=    9
   3  174    28     4  -61   108     6  105  -110     2  -78    78
H=  6, K=    8   H=  8, K=    8   H=  2, K=    8   H=  4, K=    9
   3  -84   -81     4  -81    -4     6  -77     2     2  -77   -24
H=  7, K=    8   H=  9, K=    8   H=  3, K=    8   H=  5, K=    9
   3  -23    28     4  172  -146     6  -77    -0     2  -78   -23
H=  8, K=    8   H= 10, K=    8   H=  0, K=    9   H=  6, K=    9
   3  -23   -57     4  -88  -148     0  189   207     2  110   -55
H=  9, K=    8   H= 11, K=    8   H=  1, K=    9   H=  1, K=    9
   3  137  -167     4  -77    10     0  -70   -14     3  -77    88
H= 10, K=    8   H= 12, K=    8   H=  2, K=    9   H=  2, K=    9
   3  -20   -55     4  171  -104     0  -79   -20     3  113    80
```

APPENDIX II

CONFORMATIONAL ANALYSIS OF N-(p-BROMOPHENYL)DIMETHACRYLAMIDE BY MOLECULAR MECHANICS

Calculations on various conformations of N-(p-bromophenyl)dimethacrylamide were performed independently by Dr. John Turner of DuPont Pioneering Research Laboratories in Wilmington, Delaware. The method used for the analysis was a molecular mechanics method, which is based upon classical internal parameters such as bond lengths, bond angles and torsional angles. The computational schemes require the choice and calibration of functions and parameters using experimental data from various known compounds. The application of atomic force fields is essentially, then, only an interpolation from those known compounds. After initial input of these parameters the computer alters the structure by small increments in a search for the energy minimum with respect to all the variables. For a molecule with N-atoms there should then be 3N cartesian coordinates, all of which must be adjusted simultaneously to give the minimum energy. The results obtained by this method are summarized in Table 29. The ORTEP drawings of the conformers are given in Figures 16 - 19.

As to a comparison between the results obtained by Molecular Mechanics and by PCILO, reference to a review of the Molecular Mechanics method by Williams, Stang, and

Table 29

Conformational Analysis of N-(p-Bromophenyl)dimethacrylamide by Molecular Mechanics

Conformer Number	Methacryl (1)[a]	Conformation (2)	Imide (1)[a]	Conformation (2)	Energy (Kcal/mole)
1	s-trans	s-cis	trans	trans	20.725
2	s-cis	s-trans	trans	trans	20.738
3	s-cis	s-trans	trans	trans	20.719
4	skewed	s-cis	cis	trans	22.738
5	skewed	s-trans	cis	trans	22.368
6	skewed[b]	s-cis	cis	trans	33.724
7	skewed[c]	s-trans	cis	trans	22.358
8	skewed[d]	skewed[d]	cis	cis	30.976
9	skewed[e]	skewed[e]	cis	cis	30.499
10	skewed[f]	skewed	cis	cis	29.263
11		crystal coordinates			260.2
12		crystal conformer (minimized)			23.236

[a] Corresponds to methacryl group denoted by (') in PCILO calculations

[b] Different from conformer (4) by 180° rotation around the carbon-carbon single bond between the carbonyl and double bond

[c] Different from conformer (5) by same 180° rotation as in (b)

[d] Double bonds parallel at ~90° to the imide plane

[e] Roughly s-trans orientation of the two methacryl groups - not coplanar

[f] Double bonds parallel but 180° apart with both ~90° to the imide plane

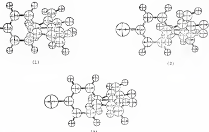


Figure 16. ORTEP Drawings of Conformers (1)-(3) with Trans-Trans Orientation of the Imide Group

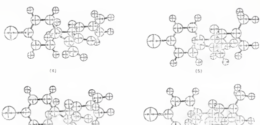
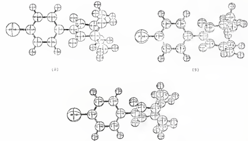


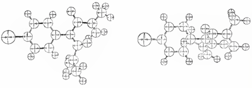
Figure 17. ORTEP Drawings of Conformers (4)-(7) with Cis-Trans Orientation of the Imide Group


(8)

(9)

(10)

Figure 18: ORTEP Drawings of Conformers (8)-(10) with Cis-Cis Orientation of the Imide Group



(11)

(12)

Figure 13: ORTEP Drawings of Conformers (11) and (12)

Schlayer[115] might be cited. In that review the pure predictive reliability of Molecular Mechanics was questioned. Though results have been obtained with a fairly good degree of accuracy the calculations are based on a rather large number of adjustable parameters. Extension from available data to new compounds must necessarily involve the introduction of new parameters whose choice is usually specific for that particular new compound. Applications of the method, therefore, are generally the most successful when applied to compounds that do not differ widely from those for which the parameters had been evaluated. The authors also remarked[115] that simplified quantum-mechanical treatments such as extended Huckel methods should be the fundamentally preferred method which should provide the most detailed and reliable information.

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BIOGRAPHICAL SKETCH

Sharon Arlene Stone was born on May 10, 1951 in Martinsville, Virginia, where the nearest hospital was located. She was the second of five children born to Irvin and Geneve Stone. Since their home was in Bassett, Virginia, she attended John D. Bassett High School and graduated from there in June, 1969.

In September, 1969, she enrolled in undergraduate school at Emory and Henry College, a small liberal arts college in the hills of Virginia. In June, 1973, she graduated magna cum laude with a Bachelor of Science degree with a major in chemistry and interdisciplinary minor in math and physics.

Graduate school began for her the following fall when she entered the Department of Chemistry at the University of Florida. While a teaching assistant during her four and a half years in graduate school she was awarded a DuPont Teaching Award and a Graduate School Teaching Fellowship.

In December, 1977, she became engaged to marry Dr. Nils Elander of Stockholm, Sweden. After a May wedding they will pursue their respective careers in Sweden

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

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George B. Butler, Chairman
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William R. Dolbier
Professor of Chemistry

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This dissertation was submitted to the Graduate Faculty of the Department of Chemistry in the College of Arts and Sciences and to the Graduate Council, and was accepted as partial fulfillment of the requirements for the degree of Doctor of Philosophy.

June, 1978

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